

exothermic process

|ɪ'eksəʊ 'THərmik 'prōses|

heat of combustion

|hēt əv kəm'bəsCH(ə)n|

endothermic process

|'ɛndəʊ 'THərmik 'prōses|

Kirchhoff's law |'kɪətʃfɔ:l|

Key Principles

- Chemical or physical change is *always* accompanied by a change in the energy content of the matter. (*Introduction*)
- To study a *change in energy* (ΔE), scientists conceptually divide the universe into the *system* (the part being studied) and the *surroundings* (everything else). All energy changes occur as *heat* (q) and/or *work* (w), transferred either from the surroundings to the system or from the system to the surroundings ($\Delta E = q + w$). Thus, the total energy of the universe is constant (*law of conservation of energy, or first law of thermodynamics*). (*Section 1.1*)
- Because E is a *state function*—a property that depends *only* on the current state of the system— ΔE depends only on the difference between the initial and final values of E . Therefore, the magnitude of ΔE is the same no matter how a given change in energy occurs. (*Section 1.1*)
- Enthalpy* (H) is also a state function and is related to E . The *change in enthalpy* (ΔH) equals the heat transferred at constant pressure, q_P . Most laboratory, environmental, and biological changes occur at constant P , so ΔH is more relevant than ΔE and easier to measure. (*Section 1.2*)
- The *change in the enthalpy of a reaction* (ΔH_{rxn}) is negative (< 0) if the reaction releases heat (*exothermic*) and positive (> 0) if it absorbs heat (*endothermic*). (*Section 1.2*)
- The more heat a substance absorbs, the higher its temperature becomes, but each material has its own *capacity* for absorbing heat. Knowing this capacity and measuring the change in temperature in a *calorimeter*, we can find ΔH_{rxn} . (*Section 1.3*)
- The quantity of heat released or absorbed in a reaction is related *stoichiometrically* to the amounts (mol) of reactants and products. (*Section 1.3*)
- Because H is a state function, we can find ΔH of any reaction by imagining the reaction occurring as the sum of other reactions whose enthalpies of reaction we know or can measure (*Hess's law*). (*Section 1.4*)
- Chemists have specified a set of conditions, called *standard states*, to determine and compare enthalpies (and other thermodynamic variables) of different reactions. Each substance has a *standard enthalpy of formation* (ΔH_f°), the enthalpy of reaction when 1 mol of the substance is formed from its elements under these conditions. The ΔH_f° values for each substance in a reaction are used to calculate the *standard enthalpy of reaction* (ΔH_{rxn}°). (*Section 1.5*)

Learning Objectives

- Interconvert energy units; understand that ΔE of a system appears as the total heat and/or work transferred to or from its surroundings; understand the meaning of a state function.
- Understand the meaning of H , why we measure ΔH , and the distinction between exothermic and endothermic reactions; draw enthalpy diagrams for chemical and physical changes.
- Understand the relation between specific heat capacity and heat transferred in both constant-pressure (coffee-cup) and constant-volume (bomb) calorimeters.
- Understand the relation between heat of reaction and amount of substance.
- Explain the importance of Hess's law and use it to find an unknown ΔH .
- View a reaction as the decomposition of reactants followed by the formation of products; understand formation equations and how to use ΔH_f° values to find ΔH_{rxn}° .



USTH

Chapter 1: Thermochemistry: Energy Flow & Chemical Change

Dr. Truong Thanh Tu
VNU University of Science
334 Nguyen Trai, Thanh Xuan, Hanoi
tuthanhtruong@gmail.com

<http://moodle.usth.edu.vn/enrol/index.php?id=321>


Thermochemistry: Energy Flow & Chemical Change

- 1.1 Forms of Energy and Their Interconversion
- 1.2 Enthalpy: Chemical Change at Constant Pressure
- 1.3 Calorimetry: Measuring the Heat
- 1.4 Hess's Law: Finding ΔH of Any Reaction
- 1.5 Standard Enthalpies of Reaction (ΔH°_{rxn})

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1.1 Forms of Energy and Their Interconversion

- All changes in matter are accompanied by changes in energy.
 - Some reactions **release energy**, e.g. burning wood.
 - Some reactions **require energy**, e.g. photosynthesis.




- **Thermodynamics** is the study of energy and its transformations.
- **Thermochemistry** is a branch of thermodynamics that deals with the heat involved in chemical and physical changes.

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The Nature of Energy

- **Energy**: The capacity to supply heat or do work.
 - **Kinetic Energy (E_K)**: The energy of motion.
- $$KE = \frac{1}{2}mv^2$$
- **Potential Energy (E_P)**: Stored energy (due to position or composition).
 - When energy is transferred from one object to another, it appears as **work** and/or **heat**.
 - **Work (w)**: energy transferred when an object is *moved by force*
 - **Heat (q)**: Energy transferred between objects due to a *temperature difference*

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Units of Energy

- The SI unit of energy is the **joule (J)**.
 $1\text{ J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2$
- The **calorie** was once defined as the quantity of energy needed to raise the temperature of 1 g of water by 1 °C.
 $1\text{ cal} = 4.184\text{ J}$
- The **British Thermal Unit (Btu)** is often used to rate appliances.
1 Btu is equivalent to 1055 J.

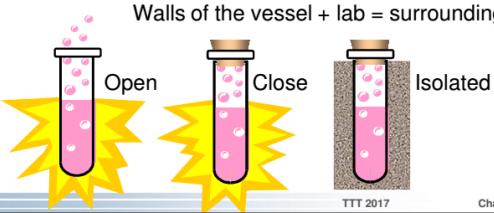
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The System and Its Surroundings

- A meaningful study of any transfer of energy requires that we first clearly define both the **system** and its **surroundings**.
- In thermodynamics the **universe** is divided into two parts:
 - the **system** = what we're interested in measuring
 - the **surroundings** = everything else (which could affect the system)
- **System + Surroundings = Universe**

Contents of a reaction vessel = system
Walls of the vessel + lab = surroundings

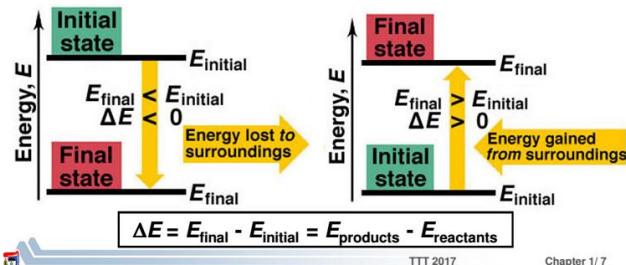


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Internal Energy, E (sometimes U)

- Internal energy of a system = sum of kinetic and potential energies of all 'particles' contained in it.
- A change in the energy of the system must be accompanied by an equal and opposite change in the energy of the surroundings.



State Functions

- The state of a chemical system is characterized by a set of parameters, including T (temperature), P (pressure), and V (volume).
 - Changes of the system's state:
- (1) T_1, P_1, V_1 (2) T_2, P_2, V_2
- State Function:** A function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state.
 - Internal energy, E , is a state function.

The Law of Energy Conservation

- The first law of Thermodynamics states that the total energy of the universe is constant.
- A chemical reaction always involves a transfer of energy between the system and the surroundings.

$$\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$$

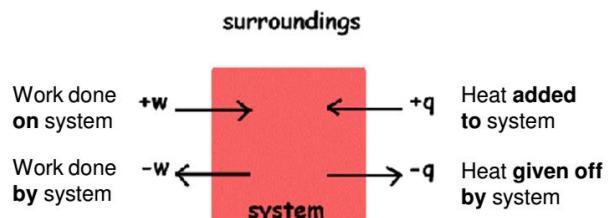
- Energy is conserved, and is neither created nor destroyed. Energy is transferred in the form of heat and/or work.
- Because energy transfer can only occur in these two forms, the total change in the system's internal energy (ΔE) is therefore:

$$\Delta E = q + w$$

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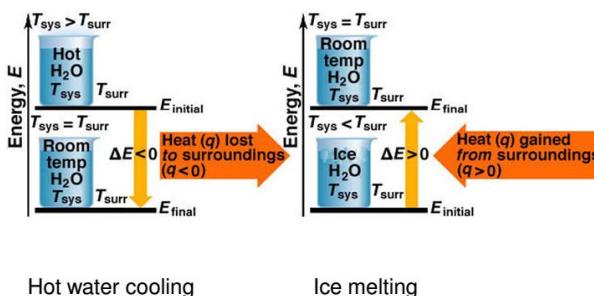
Heat and Work

- The sign of q and w can be positive or negative depending on the change the system undergoes.
- If the system loses heat to the surroundings, q is negative.
- If the system does work on the surroundings, w is negative.



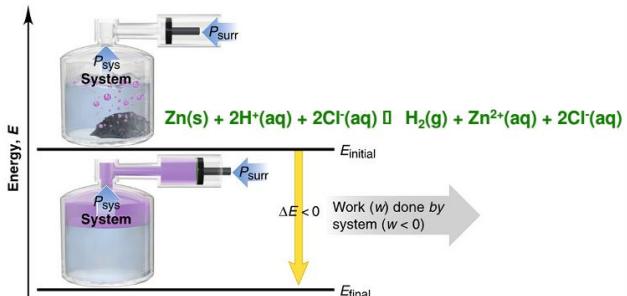
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Energy Transfer as Heat Only



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Energy Transfer as Work Only



In this example a volume change occurs against an external pressure. This is a particularly important and useful form of work. It is given the name Pressure-Volume work (PV work).

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Forms of Work

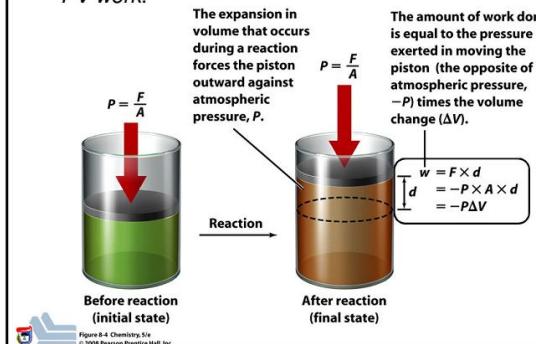
- The most important forms of work are:
 - PV work** = expansion of a gas
(e.g. steam engine)
 - Electrical work** = movement of charged particles
(e.g. in a battery)



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Expansion Work

Expansion Work: Work done as the result of a volume change in the system. Also called *pressure-volume* or *PV work*.



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Work, Pressure, and Volume

$$w = -P\Delta V$$

Expansion

$+ \Delta V$ (increase)

\downarrow

$-w$ results

\downarrow

E_{system} decreases

\downarrow

Work has been done **by** the system on the surroundings

Compression

$- \Delta V$ (decrease)

\downarrow

$+w$ results

\downarrow

E_{system} increases

\downarrow

Work has been done **on** the system by the surroundings

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The Sign Conventions* for q , w , and ΔE

q	$+$	w	$=$	ΔE
+		+		+
+		-		depends on sizes of q and w
-		+		depends on sizes of q and w
-		-		-

* For q : + means system **gains** heat; – means system **releases** heat.

* For w : + means work done **on** system; – means work done **by** system.

Applying in Thermodynamic Processes

$$\Delta E = q + w$$

$q =$ heat transferred

$w =$ work = $-P\Delta V$

▪ **Isobaric process** (constant pressure): $P_1 = P_2$

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

▪ **Isochoric process** (constant volume): $\Delta V = 0$

$$q_v = \Delta E$$

▪ **Isothermal process** (constant temperature): $\Delta E = 0$

$$q = -w$$

▪ **Adiabatic process** (no heat transferred): $q = 0$

$$\Delta E = w$$

$q_p = q_v + P\Delta V \rightarrow$ Reactions w. solids, liquids ($\Delta V=0$) $\rightarrow: q_p \approx q_v$
Reactions w. gases: $q_p = q_v + \Delta nRT$

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Sample Problem 1.1

Determining the Change in Internal Energy of a System

PROBLEM: When gasoline burns in a car engine, the expanding gases do 451 J of work on the pistons and the system releases 325 J to the surroundings as heat. Calculate the change in energy (ΔE) in J, kJ, and kcal.

1.2 Enthalpy: Chemical Change at Constant P

In **chemical laboratories**, reactions are very often performed in vessels open to the atmosphere (**constant pressure**).

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

↑
Enthalpy change
or

Heat of reaction (at constant pressure)

$$H = E + PV$$

Enthalpy is a state function whose value depends only on the current state of the system, not on the path taken to arrive at that state.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

$$= H_{\text{products}} - H_{\text{reactants}}$$

Note: If any non-PV work, w' , is done $\rightarrow q_P + w' = \Delta H$

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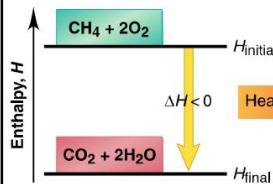
ΔH as a measure of ΔE

- ΔH is the change in heat for a system at **constant pressure**.
- $q_P = \Delta E + P\Delta V = \Delta H$
- $\Delta H \approx \Delta E$
 - for reactions that do not involve gases
e.g. $\text{OH}^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l)$
 - for reactions in which the total amount (mol) of gas does **not** change
e.g. $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$
 - for reactions in which q_P is much larger than $P\Delta V$, even if the total mol of gas does change.
e.g. $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$

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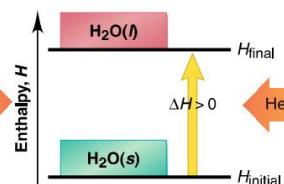
Exothermic vs. Endothermic Reactions



A Exothermic process

Heat is **released** to the surroundings.
 $H_{\text{final}} < H_{\text{initial}}$, $\Delta H < 0$

e.g. Combustion of methane,
 $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
+ heat



B Endothermic process

Heat is **absorbed** from the surroundings.
 $H_{\text{final}} > H_{\text{initial}}$, $\Delta H > 0$

e.g Melting of ice
 $\text{H}_2\text{O}(s) + \text{heat} \rightarrow \text{H}_2\text{O}(l)$

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Enthalpies of Physical Changes

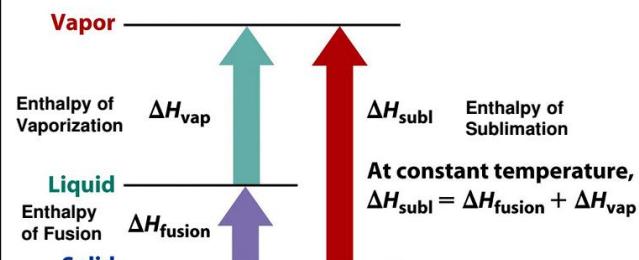


Figure 8-5 Chemistry, 5/e
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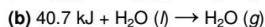
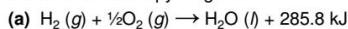
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Sample Problem 1.2

Drawing Enthalpy Diagrams and Determining the Sign of ΔH

PROBLEM: In each of the following cases, determine the sign of ΔH , state whether the reaction is exothermic or endothermic, and draw an enthalpy diagram.



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1.3 Calorimetry: Measuring the Heat

- The **heat associated with a chemical reaction** can be determined experimentally using a device called a **calorimeter**.
- **Calorimetry**, the science of measuring heat, is based on observing the **temperature change** when a body **absorbs** or **discharges** energy as heat.
- Substances respond differently to being heated.
- When a substance is heated, the **energy** required to reach a certain temperature will depend on the amount of the substance present

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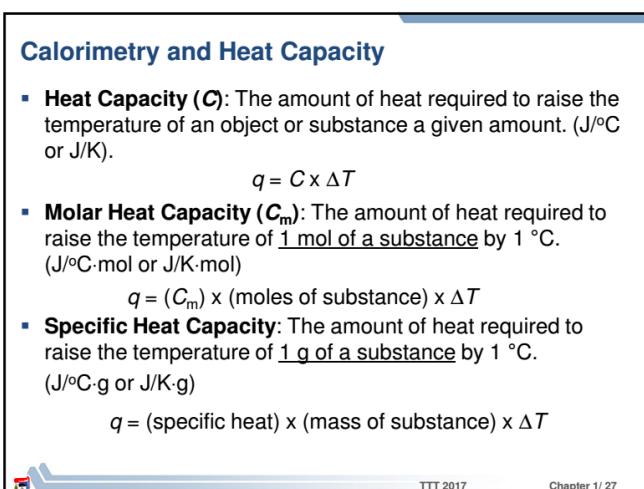
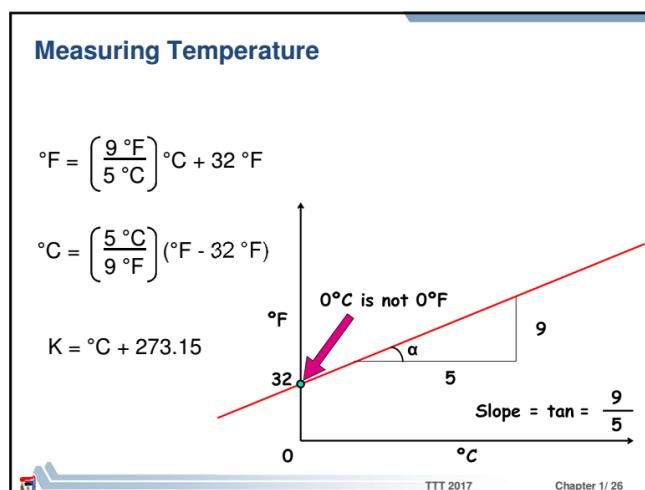
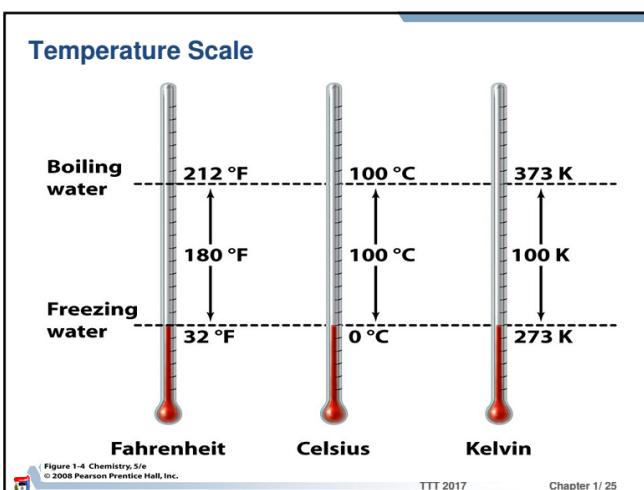


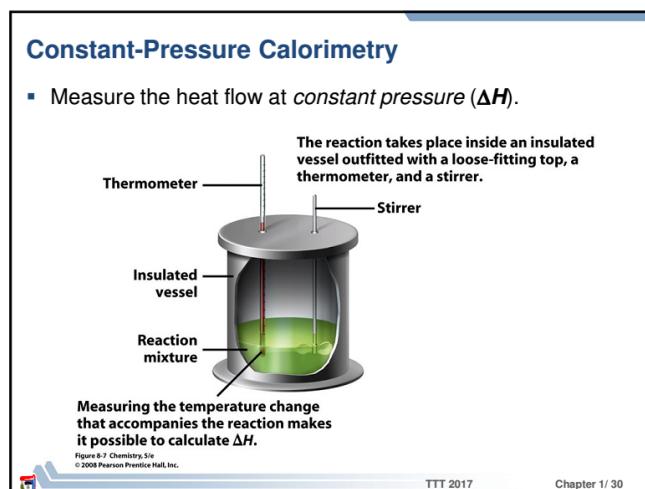
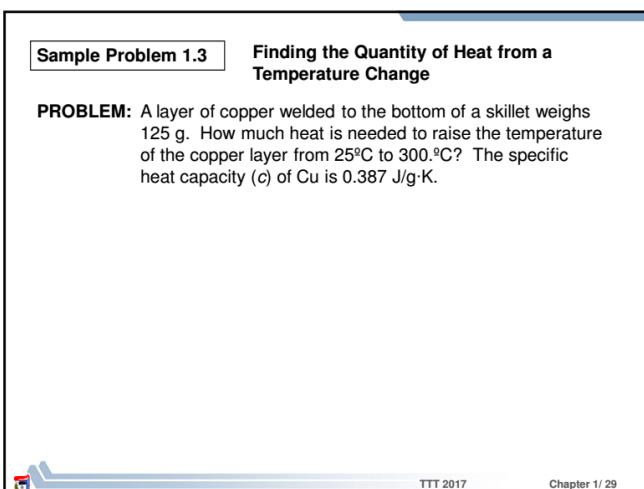
TABLE 8.1 Specific Heats and Molar Heat Capacities for Some Common Substances at 25 °C

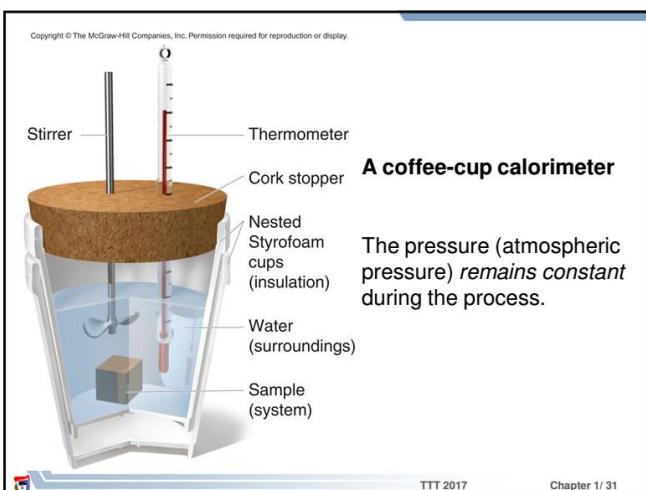
Substance	Specific Heat $\text{J}/(\text{g} \cdot ^{\circ}\text{C})$	Molar Heat Capacity $\text{J}/(\text{mol} \cdot ^{\circ}\text{C})$
Air (dry)	1.01	29.1
Aluminum	0.902	24.4
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.450	25.1
Mercury	0.140	28.0
NaCl	0.864	50.5
Water(s)*	2.03	36.6
Water(l)	4.179	75.3

* At -11°C

Table 8-1 Chemistry, 5/e
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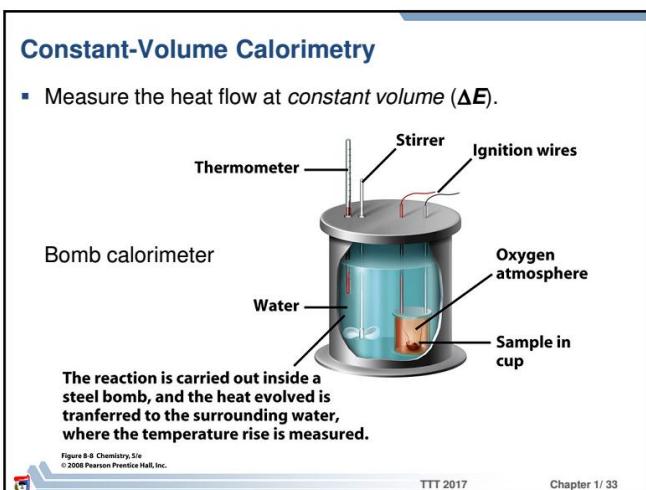
**Sample Problem 1.4****Determining the Enthalpy Change of an Aqueous Reaction**

PROBLEM: 50.0 mL of 0.500 M NaOH is placed in a coffee-cup calorimeter at 25.00°C and 25.0 mL of 0.500 M HCl is carefully added, also at 25.00°C. After stirring, the final temperature is 27.21°C. Calculate q_{soln} (in J) and the change in enthalpy, ΔH , (in kJ/mol of H_2O formed).

Assume that the total volume is the sum of the individual volumes, that $d = 1.00 \text{ g/mL}$, and that $c = 4.184 \text{ J/g}\cdot\text{K}$

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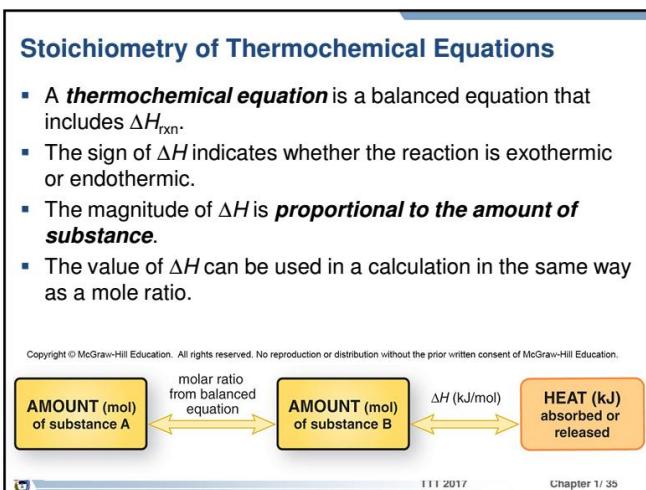
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**Sample Problem 1.5****Calculating the Heat of a Combustion Reaction**

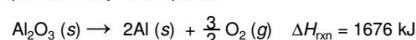
PROBLEM: A manufacturer claims that its new dietetic dessert has “fewer than 10 Calories per serving.” To test the claim, a chemist at the Department of Consumer Affairs places one serving in a bomb calorimeter and burns it in O_2 . The initial temperature is 21.862°C and the temperature rises to 26.799°C. If the heat capacity of the calorimeter is 8.151 kJ/K, is the manufacturer’s claim correct?

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**Sample Problem 1.6****Using the Enthalpy Change of a Reaction (ΔH) to Find Amounts of Substance**

PROBLEM: The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by the equation



If aluminum is produced this way, how many grams of aluminum can form when $1.000 \times 10^3 \text{ kJ}$ of heat is transferred?

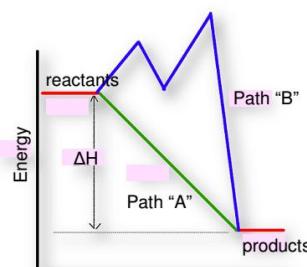
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1.4 Hess's Law: Finding ΔH of Any Reaction

Since **enthalpy** is a state function, the **change in enthalpy** in going from some initial state to some final state is *independent of the pathway*.

"In going from a particular set of **reactants** to a particular set of **products**, the **change in enthalpy (ΔH)** is the same whether the reaction takes place in one step or a series of steps."

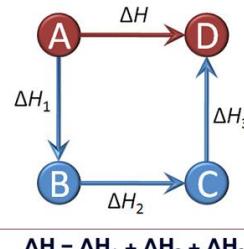


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Hess's Law

- Hess's Law:** The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.



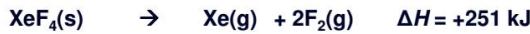
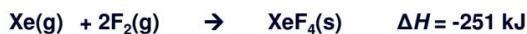
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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Rules to Use Hess's Law

- If the reaction is **reversed**, the sign of ΔH is also **reversed**.



- If coefficients are **multiplied** by an **integer**, the ΔH is also **multiplied** by **the same integer**.

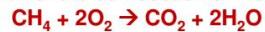


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Using Hess's Law to Calculate an Unknown ΔH

Calculate ΔH for the combustion of methane, CH_4 :



Reaction	ΔH°
$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$	-74.80 kJ
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-393.50 kJ
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-285.83 kJ
$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	+74.80 kJ

Step #1: CH_4 must appear on the reactant side, so we reverse reaction #1 and change the sign on ΔH .

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Using Hess's Law to Calculate an Unknown ΔH

Calculate ΔH for the combustion of methane, CH_4 :



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$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	+74.80 kJ
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-393.50 kJ

Step #2: Keep reaction #2 unchanged, because CO_2 belongs on the product side



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Using Hess's Law to Calculate an Unknown ΔH

Calculate ΔH for the combustion of methane, CH_4 :



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$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-393.50 kJ
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$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	+74.80 kJ
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-393.50 kJ
$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	-571.66 kJ

Step #3: Multiply reaction #3 by 2

Using Hess's Law to Calculate an Unknown ΔH

Calculate ΔH for the combustion of methane, CH_4 :



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$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$	-74.80 kJ
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$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	-571.66 kJ
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-890.36 kJ

Step #4: Sum up reaction and ΔH



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1.5 Standard Enthalpies of Reaction ($\Delta H^\circ_{\text{rxn}}$)

- Thermodynamic variables, such as ΔH , vary somewhat with conditions.
- A set of specific conditions called **standard states** is established in order to study and compare reactions:
 - For a **gas**, the standard state is **1 atm** and ideal behavior.
 - For a substance in *aqueous solution*, the standard state is **1 M** concentration.
 - For a **pure substance** (element or compound), the standard state is usually the **most stable form** of the substance at **1 atm** and the **temperature of interest**.
(That temperature is usually 25 °C (298 K).)
- When the enthalpy change of a reaction is measured at the standard state, it is the **standard enthalpy of reaction**, $\Delta H^\circ_{\text{rxn}}$ (also called *standard heat of reaction*).



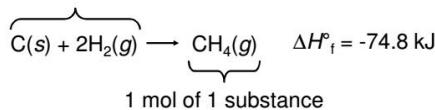
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Standard Heats of Formation

- Standard Heat of Formation (ΔH_f°):** The enthalpy change for the formation of **1 mol** of a substance in its standard state from its **constituent elements** in their **standard states**.

Standard states



- $\Delta H_f^\circ(\text{elements}) = 0$



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Table 6.3 Selected Standard Enthalpies of Formation at 25° C (298K)

Formula	ΔH_f° , (kJ/mol)	Formula	ΔH_f° , (kJ/mol)	Formula	ΔH_f° , (kJ/mol)
Calcium		Cl ₂ (g)	0	Silver	
Ca(s)	0	HCl(g)	-92.3	Ag(s)	0
CaO(s)	-635.1	Hydrogen		AgCl(s)	-127.0
CaCO ₃ (s)	-1206.9	H(g)	218.0	Sodium	
Carbon		H ₂ (g)	0	Na(s)	0
C(graphite)	0	Nitrogen		Na(g)	107.8
C(diamond)	1.9	CO(g)	-110.5	NaCl(s)	-411.1
		CO ₂ (g)	-393.5	Sulfur	
		CH ₄ (g)	-74.9	S ₈ (rhombic)	0
		CH ₃ OH(l)	-238.6	S ₈ (monoclinic)	0.3
		HCN(g)	135	Oxygen	
		CS ₂ (l)	87.9	O ₂ (g)	0
				O ₃ (g)	143
				SO ₂ (g)	-296.8
				SO ₃ (g)	-396.0
				Cl(g)	121.0
				H ₂ O(g)	-241.8
				H ₂ O(l)	-285.8

The tabulated values of ΔH_f° usually correspond to a temperature of 25 °C, but values of ΔH_f° can be obtained at any temperature.

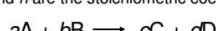
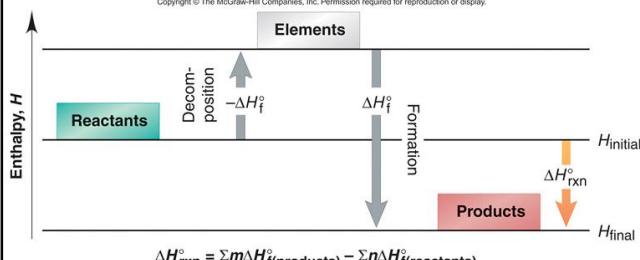


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Determining $\Delta H^\circ_{\text{rxn}}$ from ΔH_f° Values

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$$\Delta H^\circ = [c \Delta H_f^\circ(C) + d \Delta H_f^\circ(D)] - [a \Delta H_f^\circ(A) + b \Delta H_f^\circ(B)]$$

Products

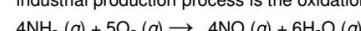
Reactants

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Sample Problem 1.7

Calculating $\Delta H^\circ_{\text{rxn}}$ from ΔH_f° Values

PROBLEM: Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:



Calculate $\Delta H^\circ_{\text{rxn}}$ from ΔH_f° values.

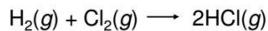


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Bond Dissociation Energies

- Bond dissociation energies** are standard enthalpy changes for the corresponding bond-breaking reactions.
- $\Delta H^\circ = D(\text{Reactant bonds}) - D(\text{Product bonds})$



$$\Delta H^\circ = (D_{\text{H-H}} + D_{\text{Cl-Cl}}) - (2D_{\text{H-Cl}})$$

$$\begin{aligned} \Delta H^\circ &= [(1 \text{ mol})(436 \text{ kJ/mol}) + (1 \text{ mol})(243 \text{ kJ/mol})] - \\ &\quad (2 \text{ mol})(432 \text{ kJ/mol}) \\ &= -185 \text{ kJ} \end{aligned}$$



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TABLE 7.1 Average Bond Dissociation Energies, D (kJ/mol)

H–H	436 ^a	C–H	410	N–H	390	O–H	460	F–F	159 ^a
H–C	410	C–C	350	N–C	300	O–C	350	Cl–Cl	243 ^a
H–F	570 ^a	C–F	450	N–F	270	O–F	180	Br–Br	193 ^a
H–Cl	432 ^a	C–Cl	330	N–Cl	200	O–Cl	200	I–I	151 ^a
H–Br	366 ^a	C–Br	270	N–Br	240	O–Br	210	S–F	310
H–I	298 ^a	C–I	240	N–I	—	O–I	220	S–Cl	250
H–N	390	C–N	300	N–N	240	O–N	200	S–Br	210
H–O	460	C–O	350	N–O	200	O–O	180	S–S	225
H–S	340	C–S	260	N–S	—	O–S	—		
Multiple covalent bonds ^b									
C=C	611	C≡C	835	C=O	732	O=O	498 ^a	N=N	945 ^a

^a Exact value^b We'll discuss multiple covalent bonds in Section 7.5.Table 7-1 Chemistry, 5/e
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Heats of Combustion

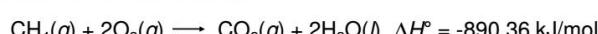


TABLE 8.3 Thermochemical Properties of Some Fuels

Fuel	Combustion Enthalpy		
	kJ/mol	kJ/g	kJ/mL
Hydrogen, H ₂	-285.8	-141.8	-9.9*
Ethanol, C ₂ H ₅ OH	-1367	-29.7	-23.4
Graphite, C	-393.5	-32.8	-73.8
Methane, CH ₄	-890.3	-55.5	-30.8*
Methanol, CH ₃ OH	-726.4	-22.7	-17.9
Octane, C ₈ H ₁₈	-5470	-47.9	-33.6
Toluene, C ₇ H ₈	-3910	-42.3	-36.7

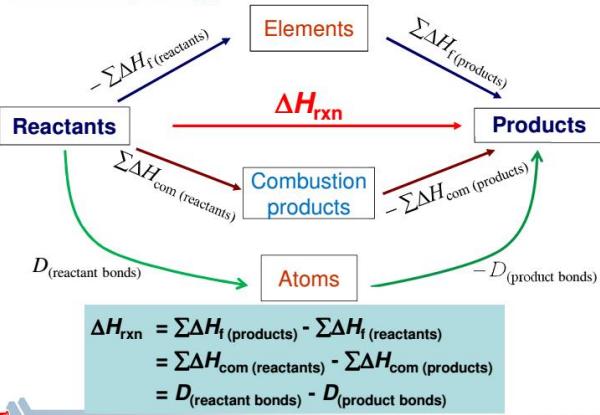
*Calculated for the compressed liquid at 0 °C

Table 8-3 Chemistry, 5/e
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Calculating ΔH_{rxn}°



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Kirchhoff's Law

- Kirchhoff's Law:** describes the enthalpy of a reaction's variation with temperature changes.

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p(T_2 - T_1)$$

Enthalpies changes at the respective temperatures

Difference in heat capacity

- ΔC_p is considered constant over a small temperature change (< 100 K).
- This allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.



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