



Schematic of Exothermic and Endothermic Processes

Hess's Law: 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.

(Nhiệt hóa học)

NHIỆT

Thermochemistry

Tất cả quá trình biến đổi qua nhiệt

(Study of heat change in
chemical or physical changes)



Energy is the capacity to do work.

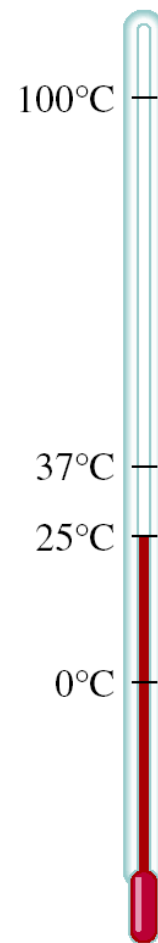
- **Radiant energy** comes from the **sun** and is earth's **primary** energy source Năng lượng bức xạ
- **Thermal energy** is the energy associated with the **random motion** of **atoms and molecules**
- **Chemical energy** is the energy stored within the **bonds** of **chemical substances**
- **Nuclear energy** is the energy stored within the **collection of neutrons and protons** in the atom
- **Potential energy** is the energy available by **virtue of an object's position** Thế năng

Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature (macroscopic manifestation) is a measure of the **thermal energy**.

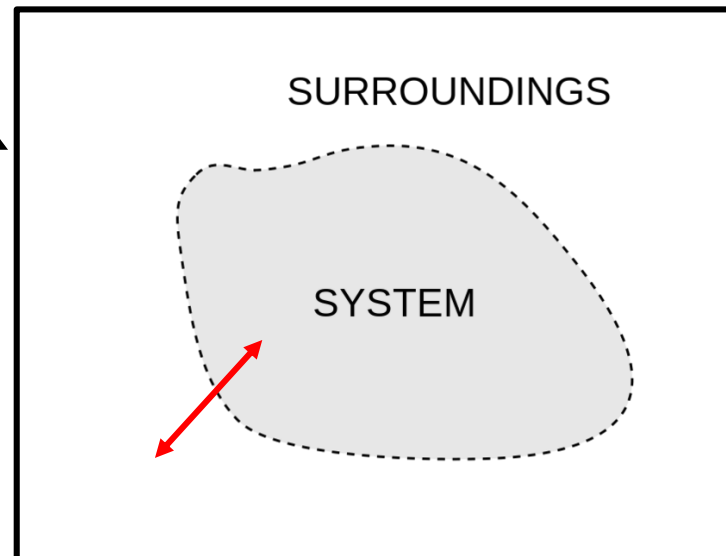
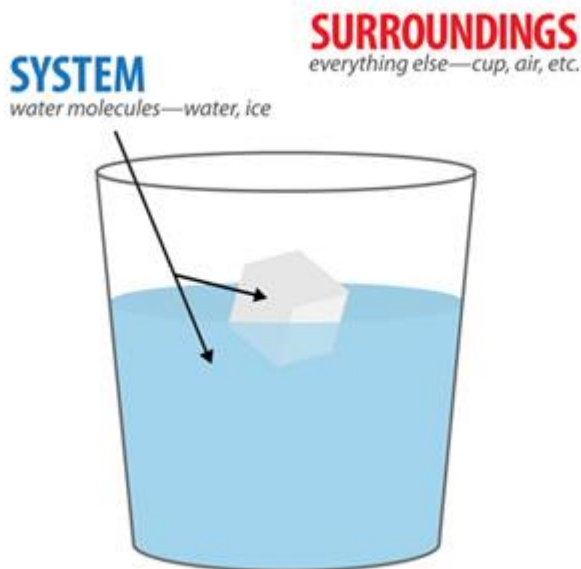
Temperature ~~≠~~ Thermal Energy



Thermochemistry is the study of heat change in chemical or physical changes.

System, surrounding, and universe

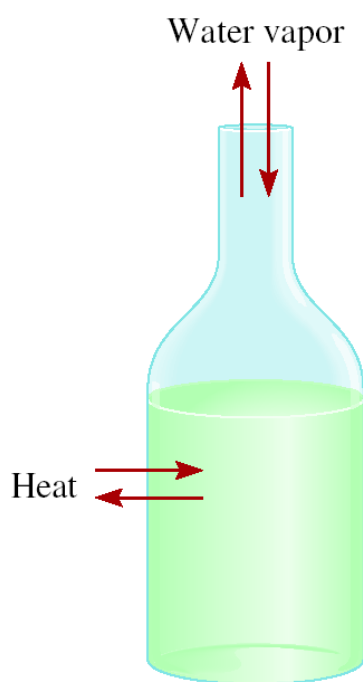
Universe = System + Surrounding



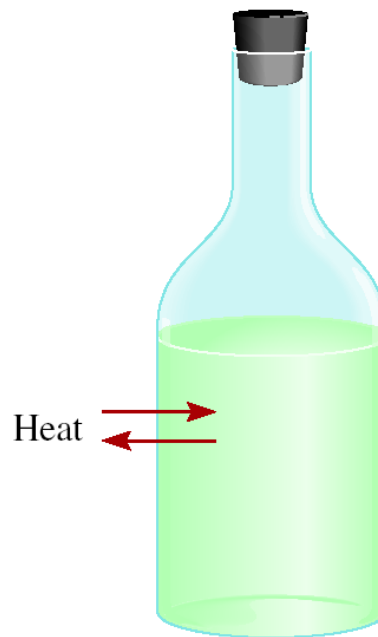
Energy flowing from one place to another during chemical or physical changes

Thermochemistry is the study of heat change in chemical reactions.

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



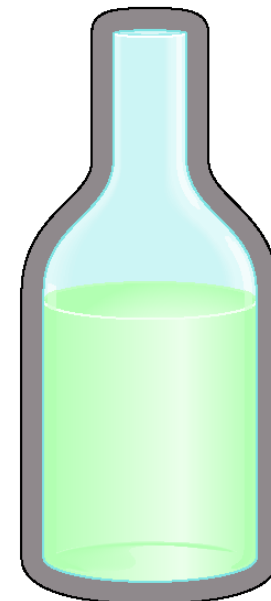
open



closed

nóng lên thôi

thermos flask, inflated balloon, air tight container



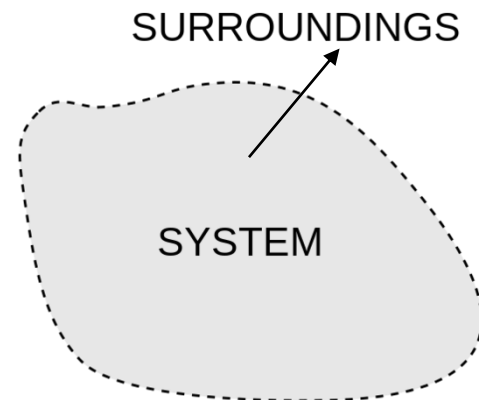
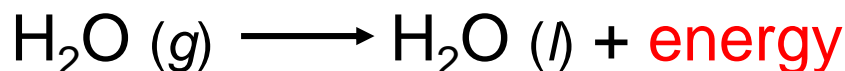
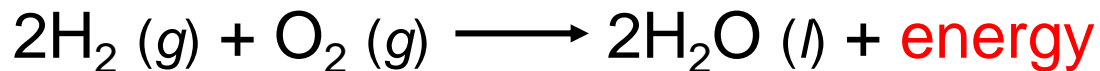
isolated

Exchange: mass & energy

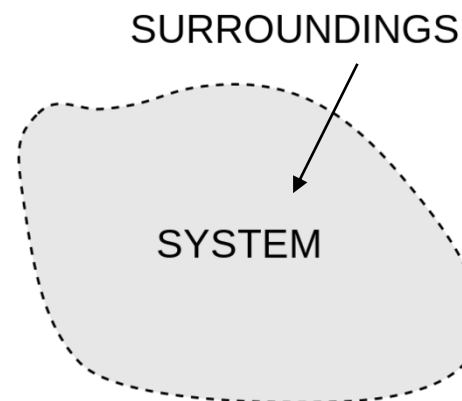
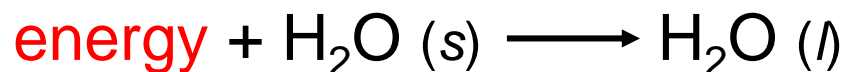
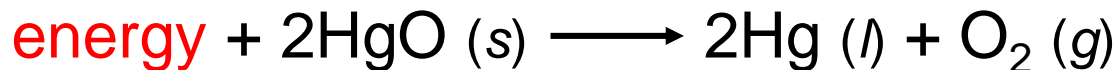
energy

nothing

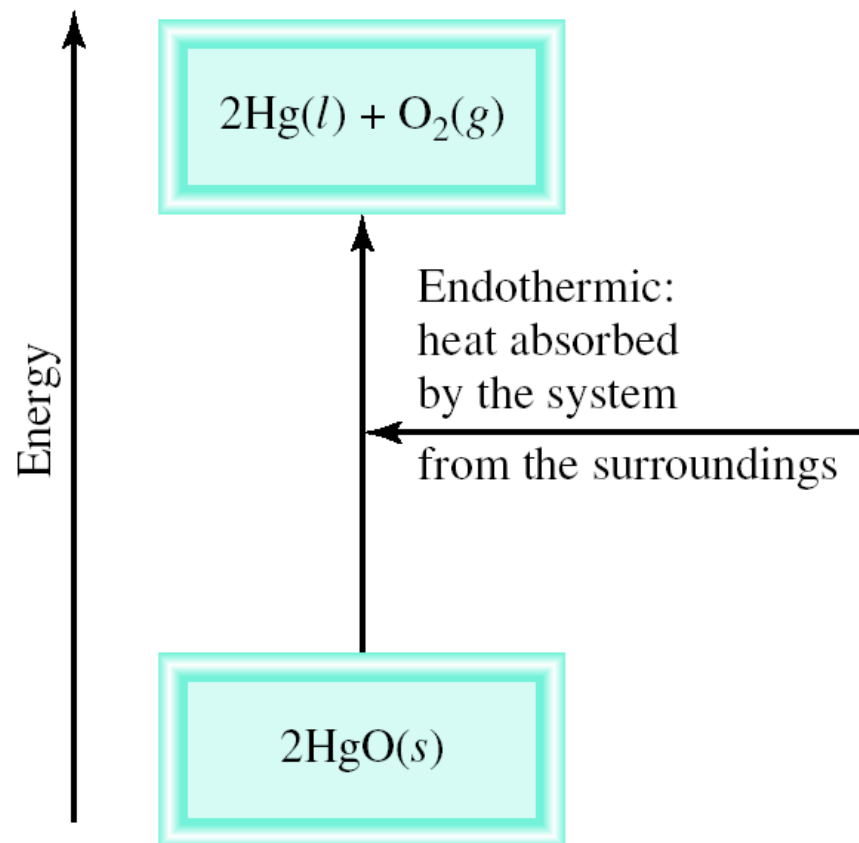
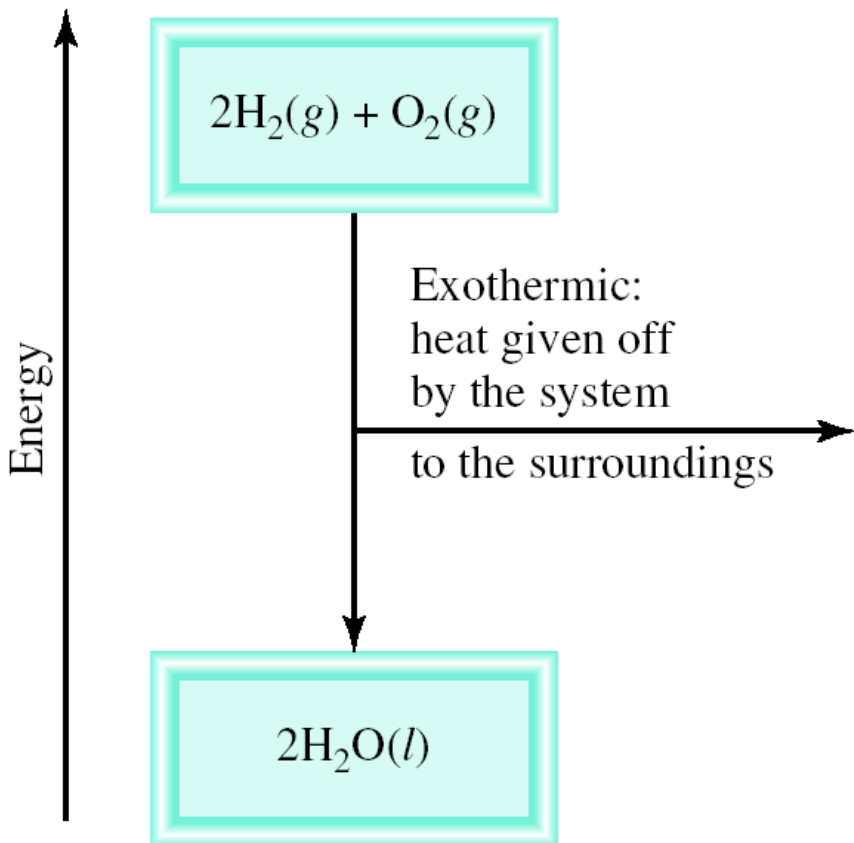
Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.



Endothermic process is any process in which heat has to be supplied to the system from the surroundings.



Schematic of Exothermic and Endothermic Processes



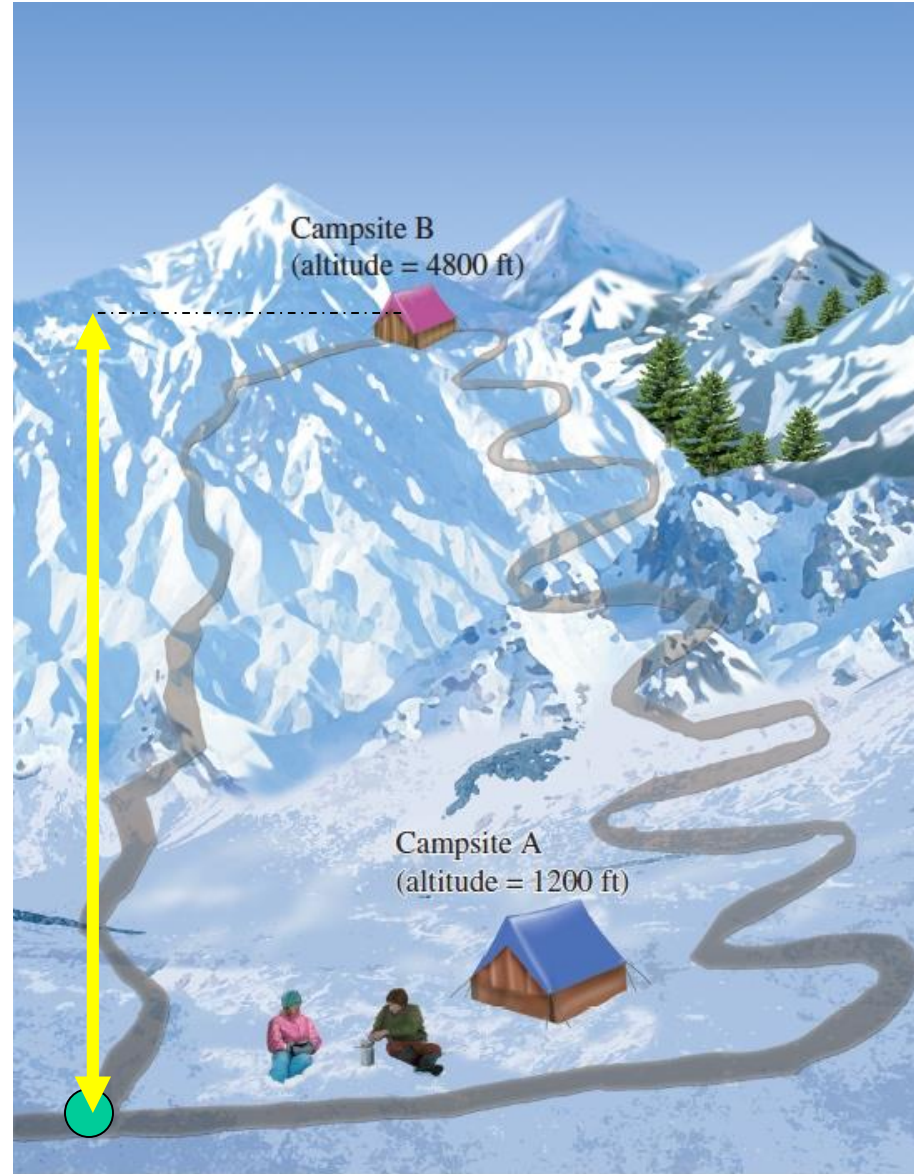
A state function is a property of a system that depends only on its present state, which is determined by variables such as temperature and pressure, and is independent of any previous history of the system.

For X to be a state function, ΔX is the same independent of how the system is changed from the initial state to the final state

$$\Delta A = A_f - A_i$$

N, T, P, V, E: State functions

The **altitude** of a campsite is a state function. It is independent of the path taken to reach it.

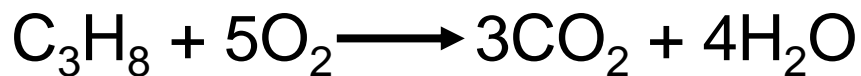
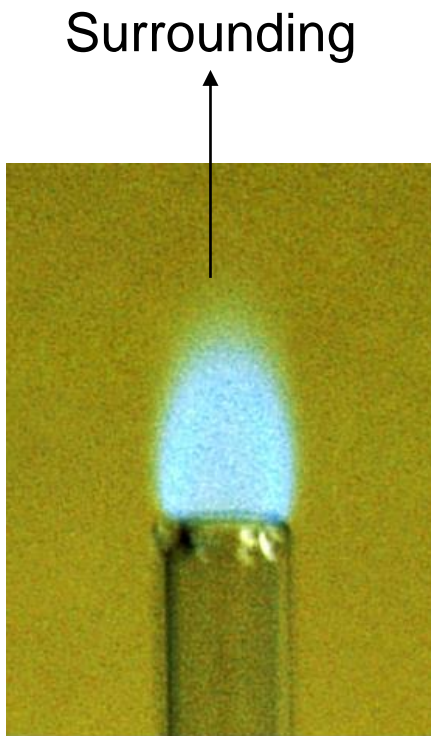


First law of thermodynamics – energy can be converted from one form to another, but cannot be created or destroyed.

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

or

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$$



Exothermic chemical reaction!

Chemical energy **lost** by combustion = Energy **gained** by the surroundings
system surroundings

Another form of the *first law* for ΔE_{system}

$$\Delta E = q + w$$

ΔE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

TABLE 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	—
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	—

Work Done On the System

$$w = F \times d$$

$$w = -P \Delta V$$

$$P \times V = \frac{F}{d^2} \times d^3 = F \times d = w$$

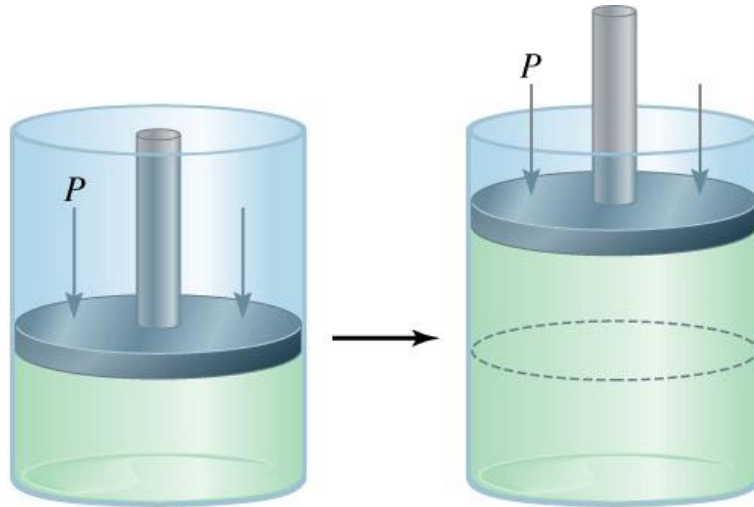
$$\Delta V > 0$$

$$-P\Delta V < 0$$

$$w_{\text{sys}} < 0$$

Work is
not a
state
function.

$$\Delta w \neq w_{\text{final}} - w_{\text{initial}}$$



initial

final

A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P \Delta V$$

$$(a) \quad \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \quad P = 0 \text{ atm}$$

$$W = -0 \text{ atm} \times 3.8 \text{ L} = 0 \text{ L}\cdot\text{atm} = 0 \text{ joules}$$

$$(b) \quad \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \quad P = 3.7 \text{ atm}$$

$$w = -3.7 \text{ atm} \times 3.8 \text{ L} = -14.1 \text{ L}\cdot\text{atm}$$

$$w = -14.1 \text{ L}\cdot\text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} = -1430 \text{ J}$$

Enthalpy and the First Law of Thermodynamics

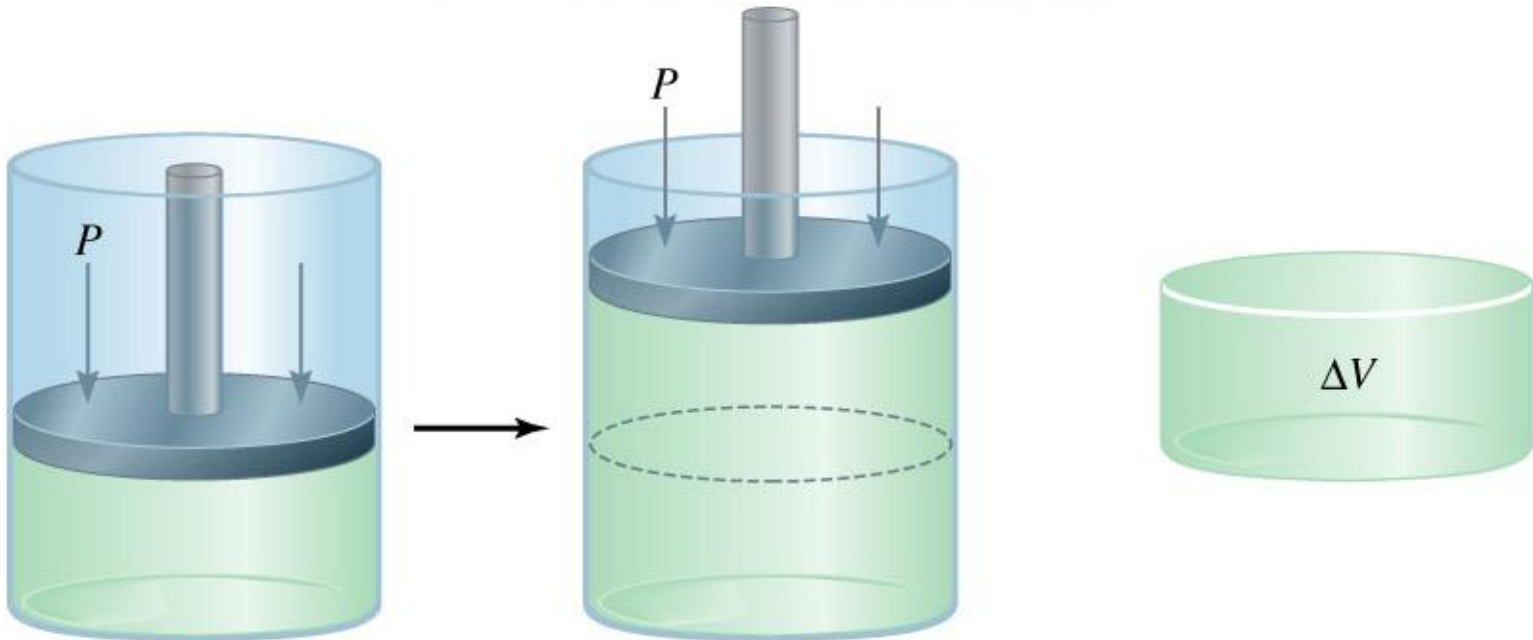
$$\Delta E = q + w$$

At constant pressure:

$$q = \Delta H \text{ and } w = -P\Delta V$$

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

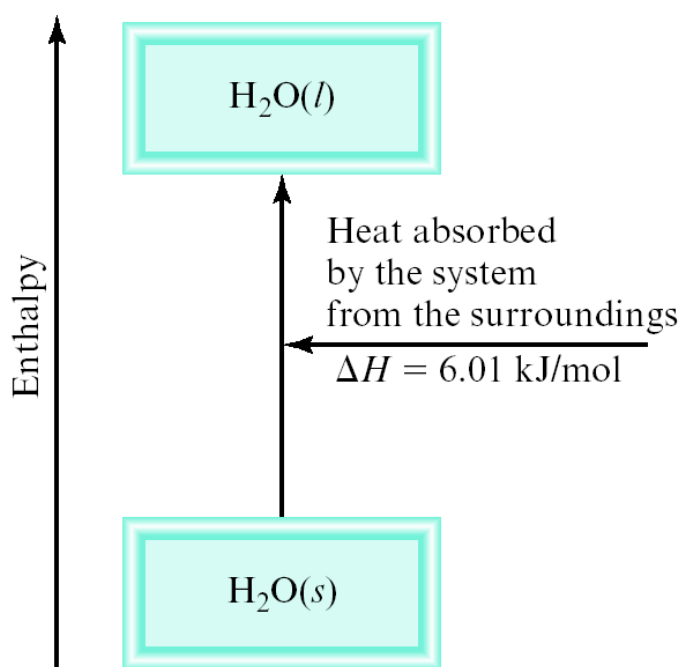
$$\Delta H = \Delta E + P\Delta V$$



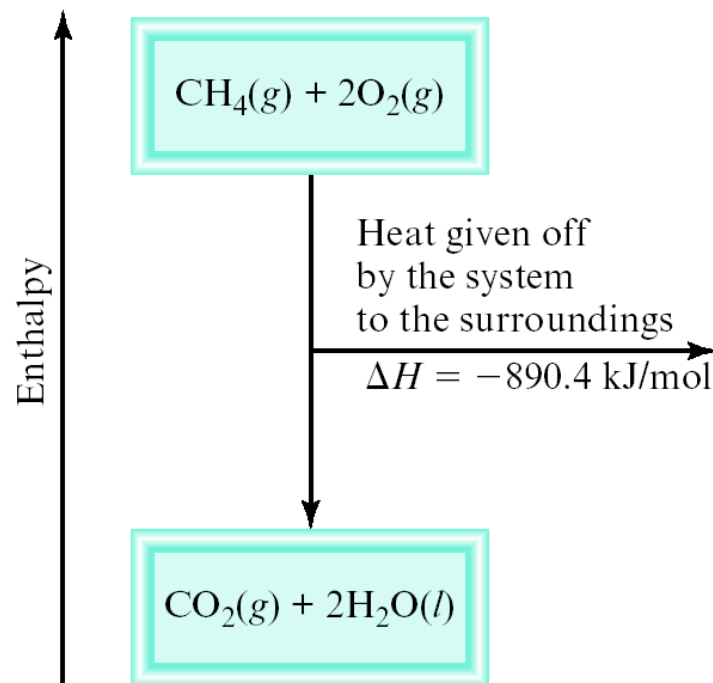
Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

ΔH = heat given off or absorbed during a reaction **at constant pressure**

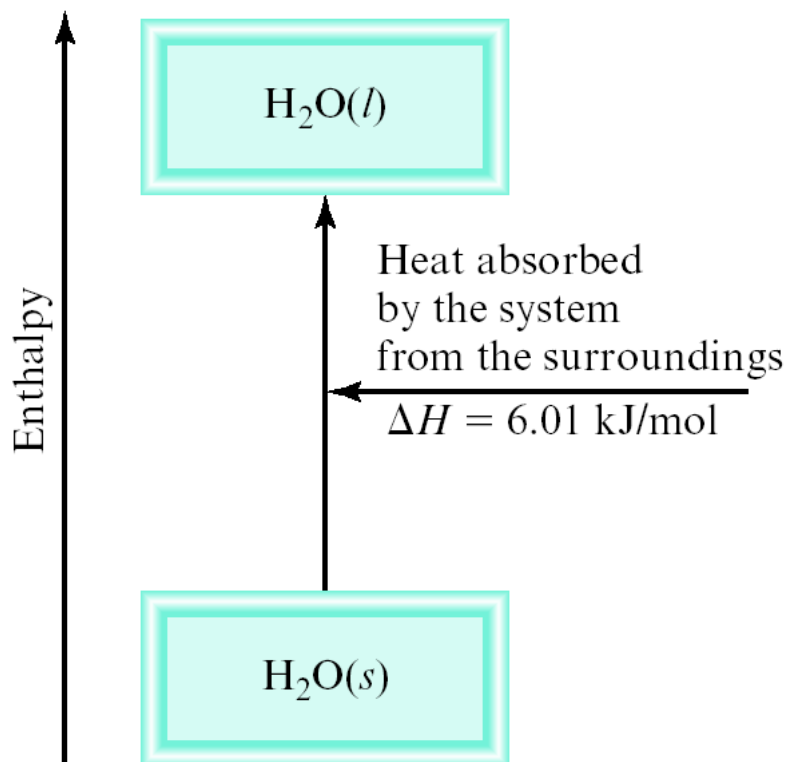


$$H_{\text{products}} < H_{\text{reactants}}$$
$$\Delta H < 0$$



$$H_{\text{products}} > H_{\text{reactants}}$$
$$\Delta H > 0$$

Thermochemical Equations



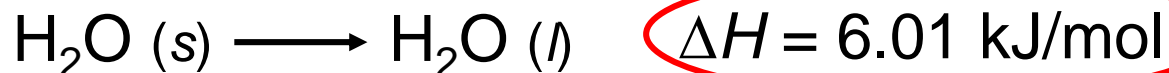
Is ΔH negative or positive?

System absorbs heat

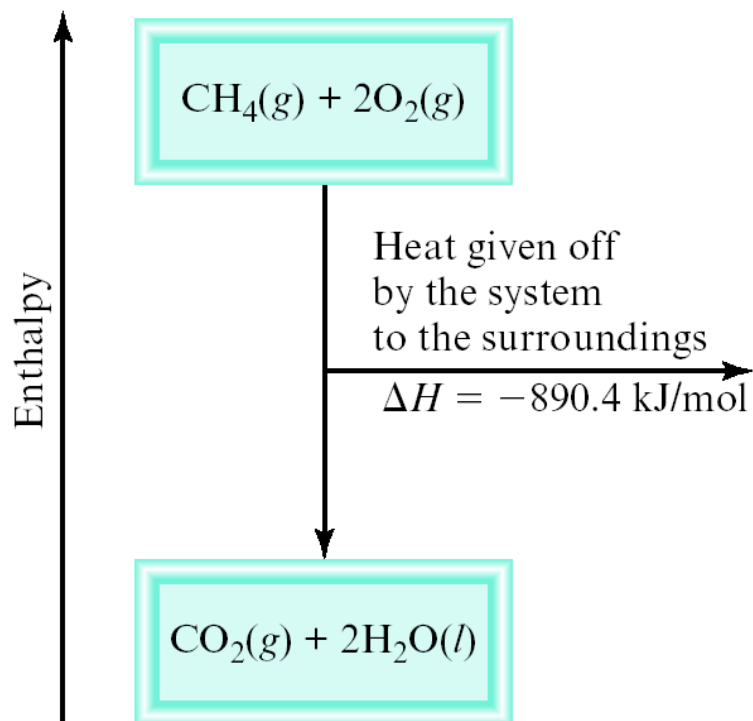
Endothermic

$$\Delta H > 0$$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0°C and 1 atm.



Thermochemical Equations



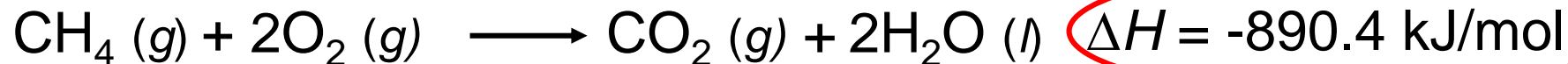
Is ΔH negative or positive?

System gives off heat

Exothermic

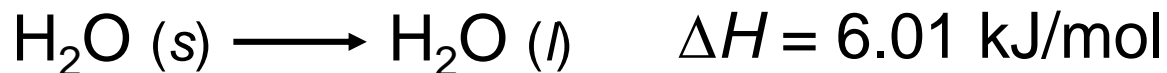
$$\Delta H < 0$$

890.4 kJ are released for every 1 mole of methane that is combusted at 25 °C and 1 atm.



Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance



- If you reverse a reaction, the sign of ΔH changes



- If you multiply both sides of the equation by a factor n , then ΔH must change by the same factor n .



Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

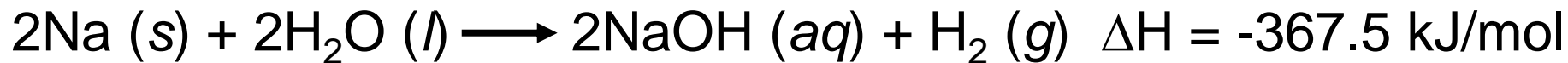


How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?



$$266 \text{ g } \cancel{\text{P}_4} \times \frac{1 \cancel{\text{ mol P}_4}}{123.9 \cancel{\text{ g P}_4}} \times \frac{3013 \text{ kJ}}{1 \cancel{\text{ mol P}_4}} = 6470 \text{ kJ}$$

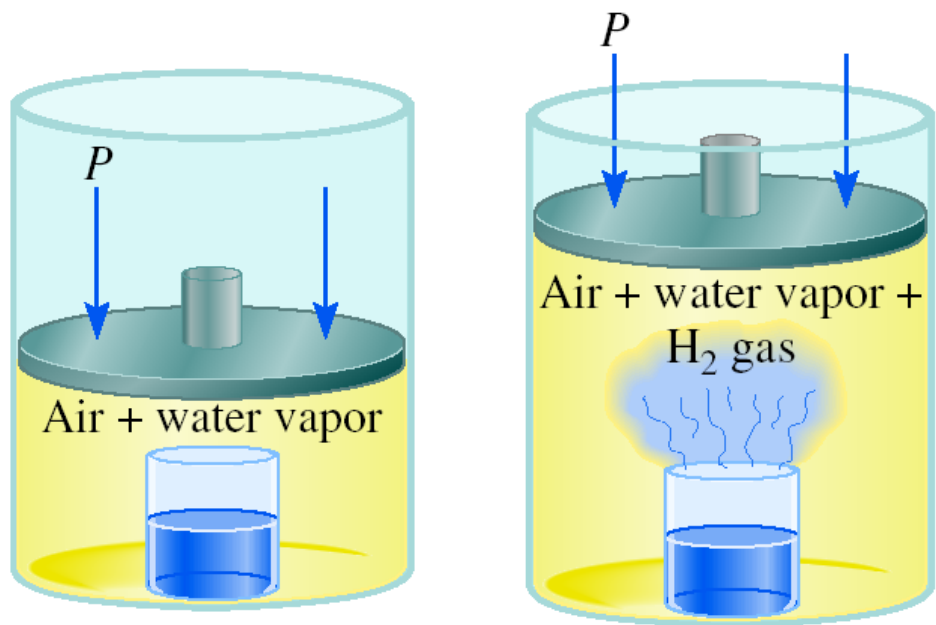
A Comparison of ΔH and ΔE



$$\Delta E = \Delta H - P\Delta V \quad \text{At } 25^\circ\text{C, 1 mole H}_2 = 24.5 \text{ L at 1 atm}$$

$$P\Delta V = 1 \text{ atm} \times 24.5 \text{ L} = 2.5 \text{ kJ}$$

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



The **specific heat** (s) of a substance is the **amount of heat** (q) required to raise the **temperature** of **one gram** of the substance by **one degree Celsius**.

The **heat capacity** (C) of a substance is the amount of heat (q) required to raise the temperature of **a given quantity** (m) of the substance by **one degree Celsius**.

TABLE 6.2

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
C ₂ H ₅ OH (ethanol)	2.46

$$C = m \times s$$

Heat (q) absorbed or released:

$$q = m \times s \times \Delta t$$

$$q = C \times \Delta t$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

How much heat is given off when an 869 g iron bar cools from 94°C to 5°C?

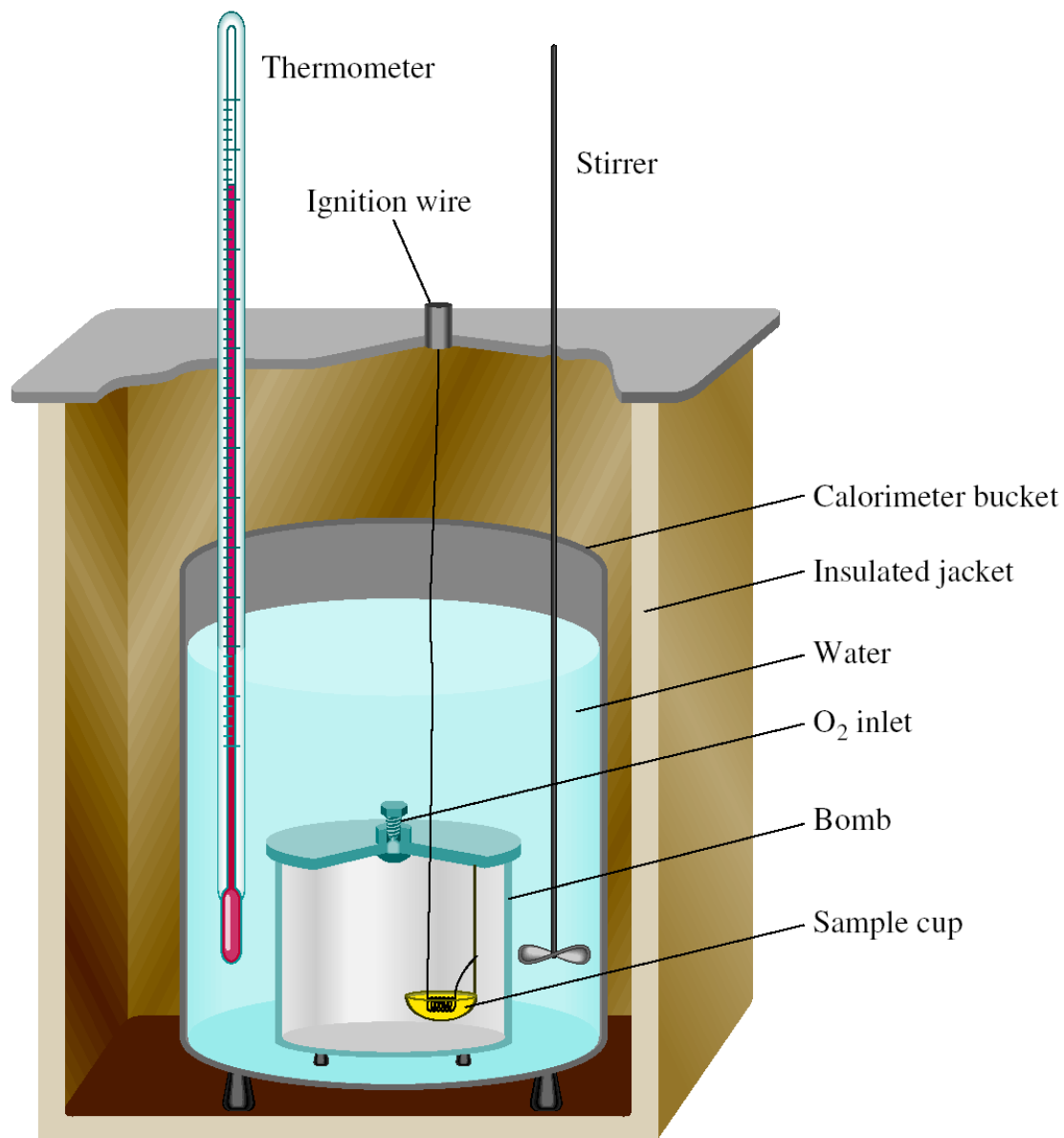
$$s \text{ of Fe} = 0.444 \text{ J/g} \cdot ^\circ\text{C}$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^\circ\text{C} - 94^\circ\text{C} = -89^\circ\text{C}$$

$$q = ms\Delta t = 869 \text{ g} \times 0.444 \text{ J/g} \cdot ^\circ\text{C} \times -89^\circ\text{C} = -34,000 \text{ J}$$



Constant-Volume Calorimetry



$$q_{\text{sys}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{bomb}})$$

$$q_{\text{water}} = m \times s \times \Delta t$$

$$q_{\text{bomb}} = C_{\text{bomb}} \times \Delta t$$

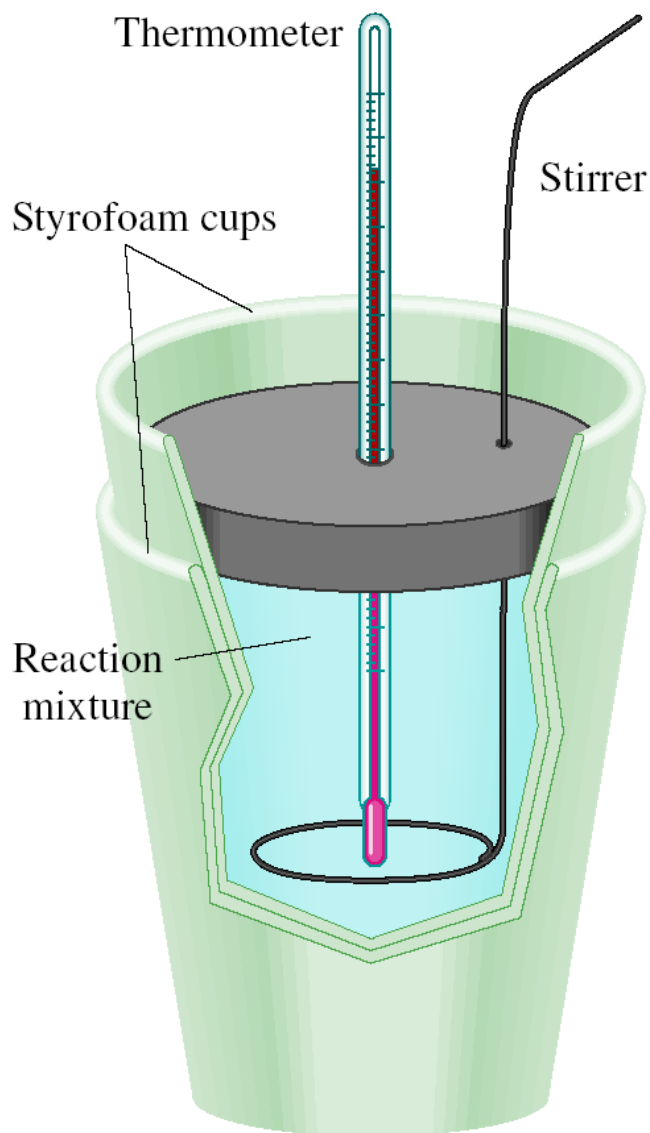
Reaction at Constant V

$$\Delta H \neq q_{\text{rxn}}$$

$$\Delta H \sim q_{\text{rxn}}$$

No heat enters or leaves!

Constant-Pressure Calorimetry



$$q_{\text{sys}} = q_{\text{water}} + q_{\text{cal}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{cal}})$$

$$q_{\text{water}} = m \times s \times \Delta t$$

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta t$$

Reaction at Constant P

$$\Delta H = q_{\text{rxn}}$$

No heat enters or leaves!

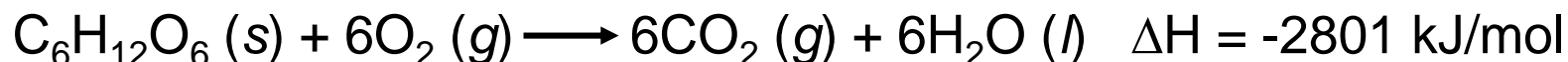
TABLE 6.3 **Heats of Some Typical Reactions Measured at Constant Pressure**

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

Chemistry in Action:

Fuel Values of Foods and Other Substances



$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}$$

Substance	$\Delta H_{\text{combustion}}$ (kJ/g)
Apple	-2
Beef	-8
Beer	-1.5
Gasoline	-34

Nutrition Facts	
Serving Size 6 cookies (28g)	
Servings Per Container about 11	
Amount Per Serving	
Calories 120	Calories from Fat 30
% Daily Value*	
Total Fat 4g	6%
Saturated Fat 0.5g	4%
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
Cholesterol 5mg	2%
Sodium 105mg	4%
Total Carbohydrate 20g	7%
Dietary Fiber Less than 1gram	2%
Sugars 7g	
Protein 2g	

Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

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

$$\Delta H_f^0 (\text{O}_2) = 0$$

$$\Delta H_f^0 (\text{O}_3) = 142 \text{ kJ/mol}$$

$$\Delta H_f^0 (\text{C, graphite}) = 0$$

$$\Delta H_f^0 (\text{C, diamond}) = 1.90 \text{ kJ/mol}$$

TABLE 6.4

Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	$\Delta H_f^\circ(\text{kJ/mol})$	Substance	$\Delta H_f^\circ(\text{kJ/mol})$
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.9
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O(g)	81.56
CaCO ₃ (s)	-1206.9	N ₂ O ₄ (g)	9.66
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-271.6	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	Zn(s)	0
H ₂ O(l)	-285.8	ZnO(s)	-348.0

The **standard enthalpy of reaction** (ΔH_{rxn}^0) is the **enthalpy** of a reaction carried out at 1 atm.

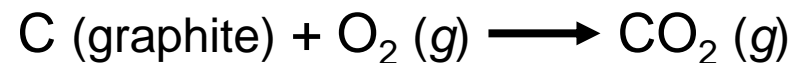
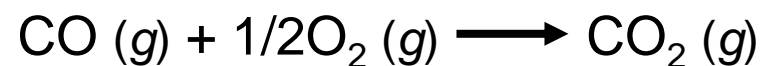
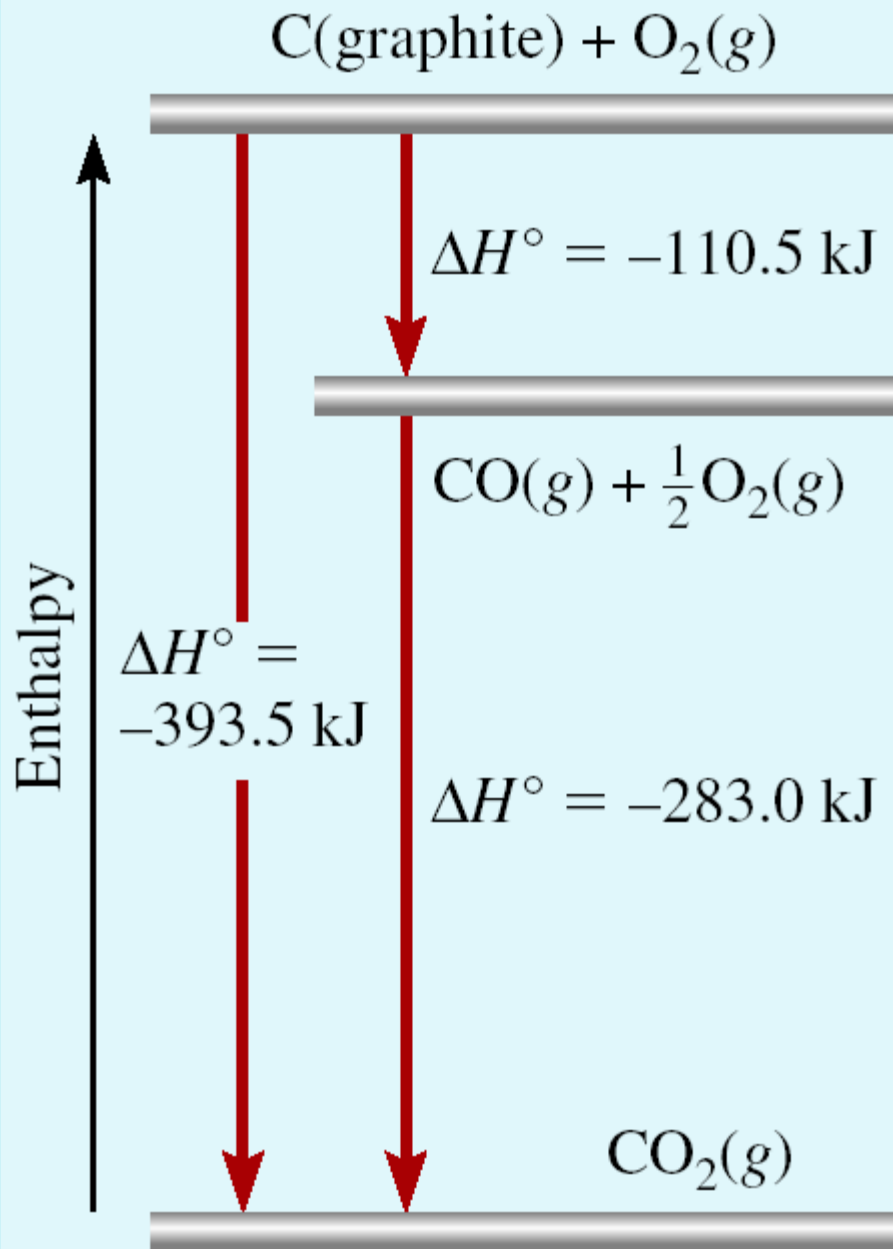


$$\Delta H_{\text{rxn}}^0 = [c\Delta H_{\text{f}}^0 (\text{C}) + d\Delta H_{\text{f}}^0 (\text{D})] - [a\Delta H_{\text{f}}^0 (\text{A}) + b\Delta H_{\text{f}}^0 (\text{B})]$$

$$\Delta H_{\text{rxn}}^0 = \Sigma n\Delta H_{\text{f}}^0 (\text{products}) - \Sigma m\Delta H_{\text{f}}^0 (\text{reactants})$$

Hess's Law: 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.

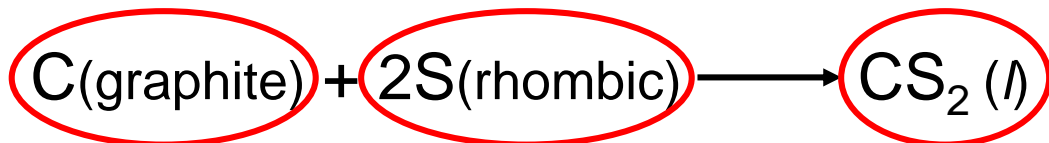
(**Enthalpy** is a state function. It doesn't matter how you get there, only where you start and end.)



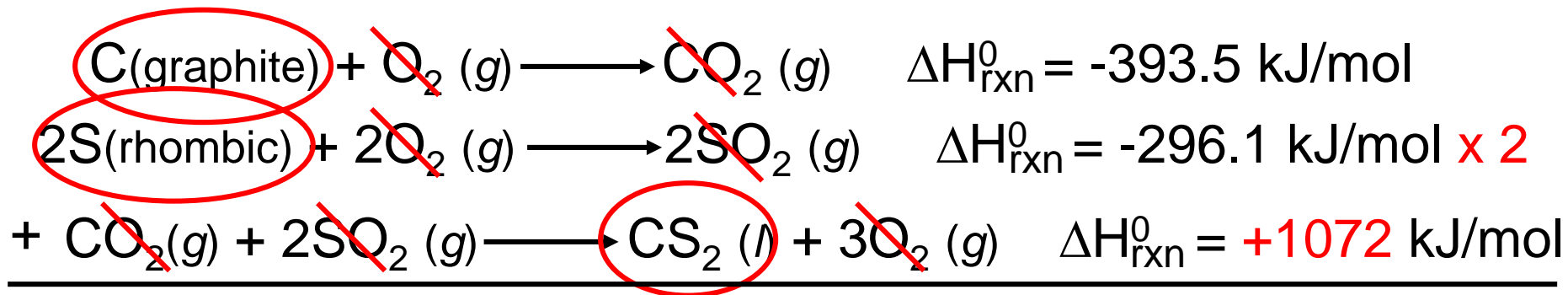
Calculate the standard enthalpy of formation of $\text{CS}_2(l)$ given that:



1. Write the enthalpy of formation reaction for CS_2

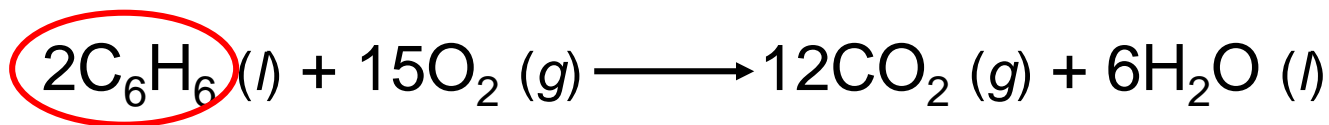


2. Add the given rxns so that the result is the desired rxn.



$$\Delta H_{\text{rxn}}^0 = -393.5 + (2 \times -296.1) + 1072 = 86.3 \text{ kJ/mol}$$

Benzene (C₆H₆) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.



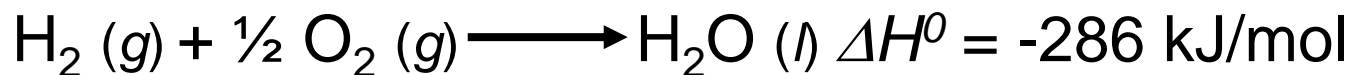
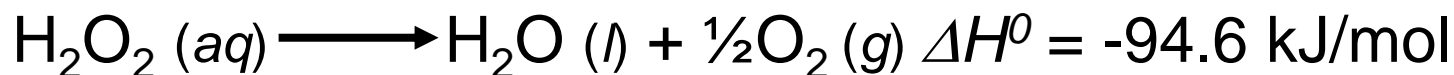
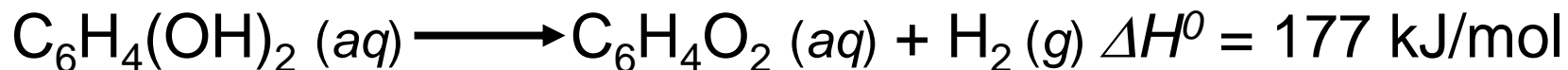
$$\Delta H_{\text{rxn}}^0 = \Sigma n\Delta H_{\text{f}}^0 (\text{products}) - \Sigma m\Delta H_{\text{f}}^0 (\text{reactants})$$

$$\Delta H_{\text{rxn}}^0 = [12\Delta H_{\text{f}}^0 (\text{CO}_2) + 6\Delta H_{\text{f}}^0 (\text{H}_2\text{O})] - [2\Delta H_{\text{f}}^0 (\text{C}_6\text{H}_6)]$$

$$\Delta H_{\text{rxn}}^0 = [12 \times -393.5 + 6 \times -187.6] - [2 \times 49.04] = -5946 \text{ kJ}$$

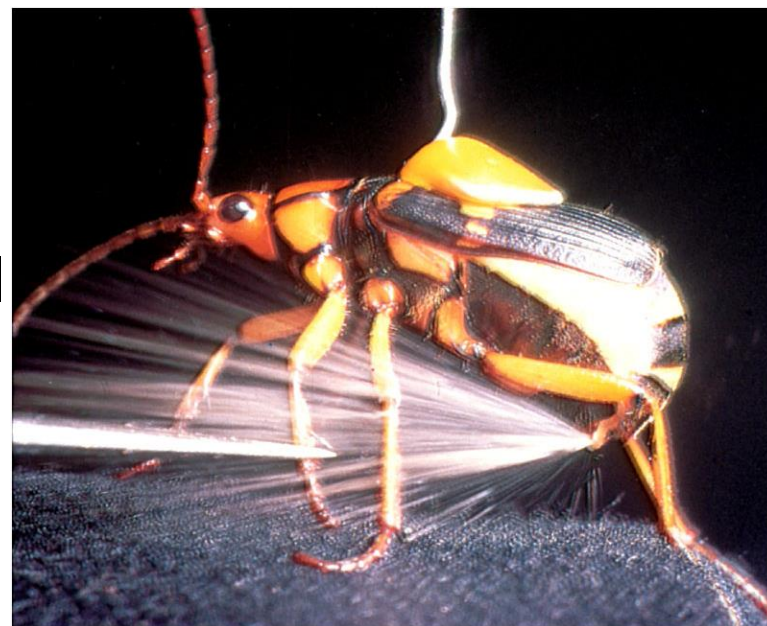
$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol C}_6\text{H}_6$$

Chemistry in Action: Bombardier Beetle Defense



$$\Delta H^0 = 177 - 94.6 - 286 = -204 \text{ kJ/mol}$$

Exothermic!



The **enthalpy of solution** (ΔH_{soln}) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}}$$

TABLE 6.5

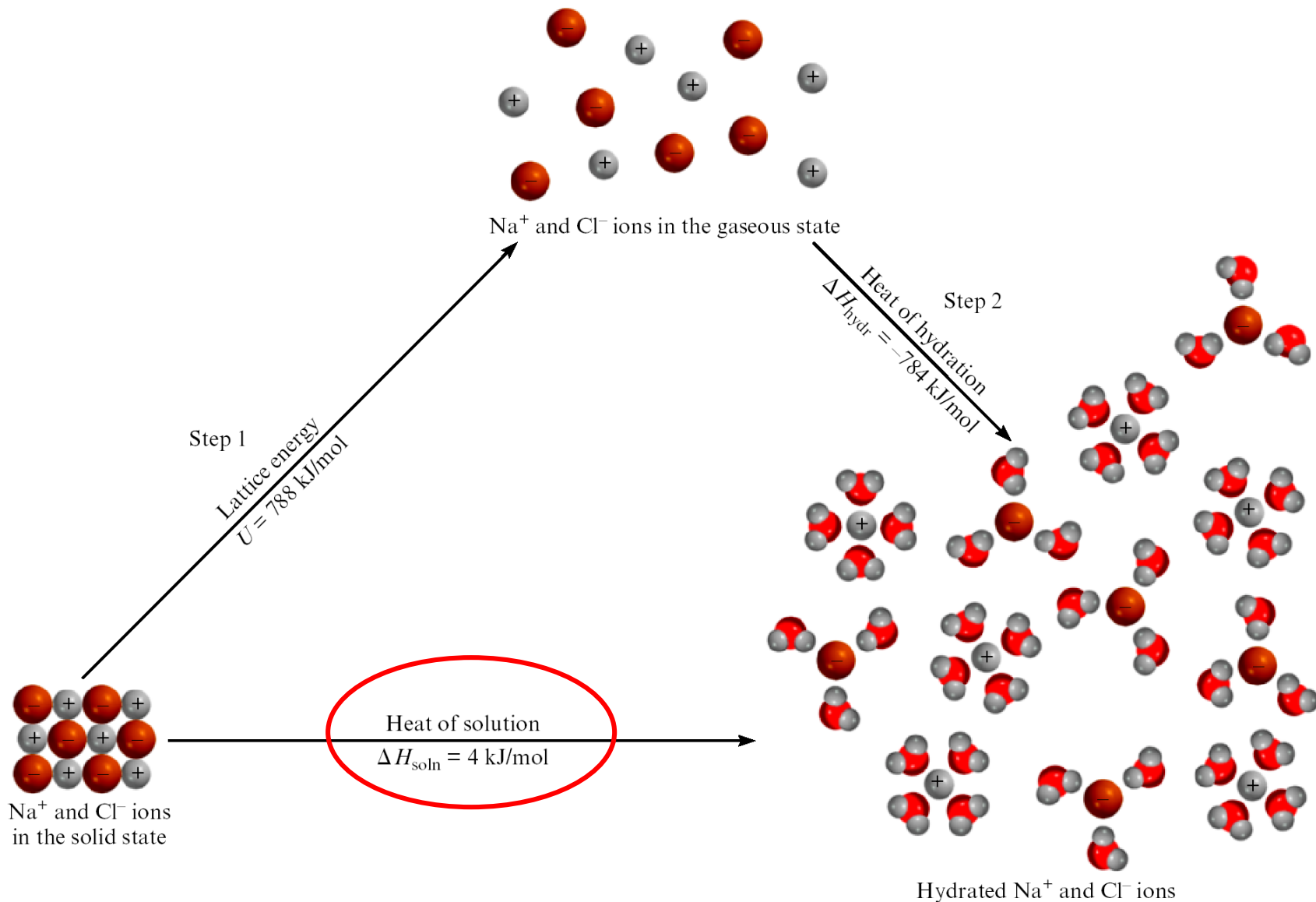
**Heats of Solution of
Some Ionic Compounds**

Compound	ΔH_{soln} (kJ/mol)
LiCl	-37.1
CaCl ₂	-82.8
NaCl	4.0
KCl	17.2
NH ₄ Cl	15.2
NH ₄ NO ₃	26.2

Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

The Solution Process for NaCl



$$\Delta H_{\text{soln}} = \text{Step 1} + \text{Step 2} = 788 - 784 = 4 \text{ kJ/mol}$$