



Thermochemistry

Chapter 6



Energy is the capacity to do work.

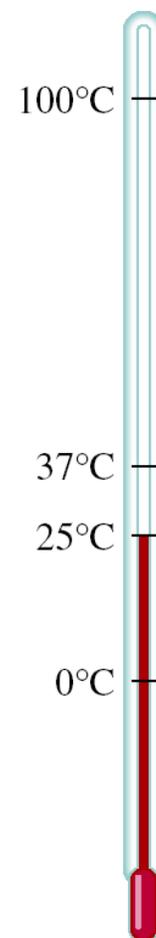
- ***Radiant energy*** comes from the sun and is earth's primary energy source
- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored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

Energy Changes in Chemical Reactions

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

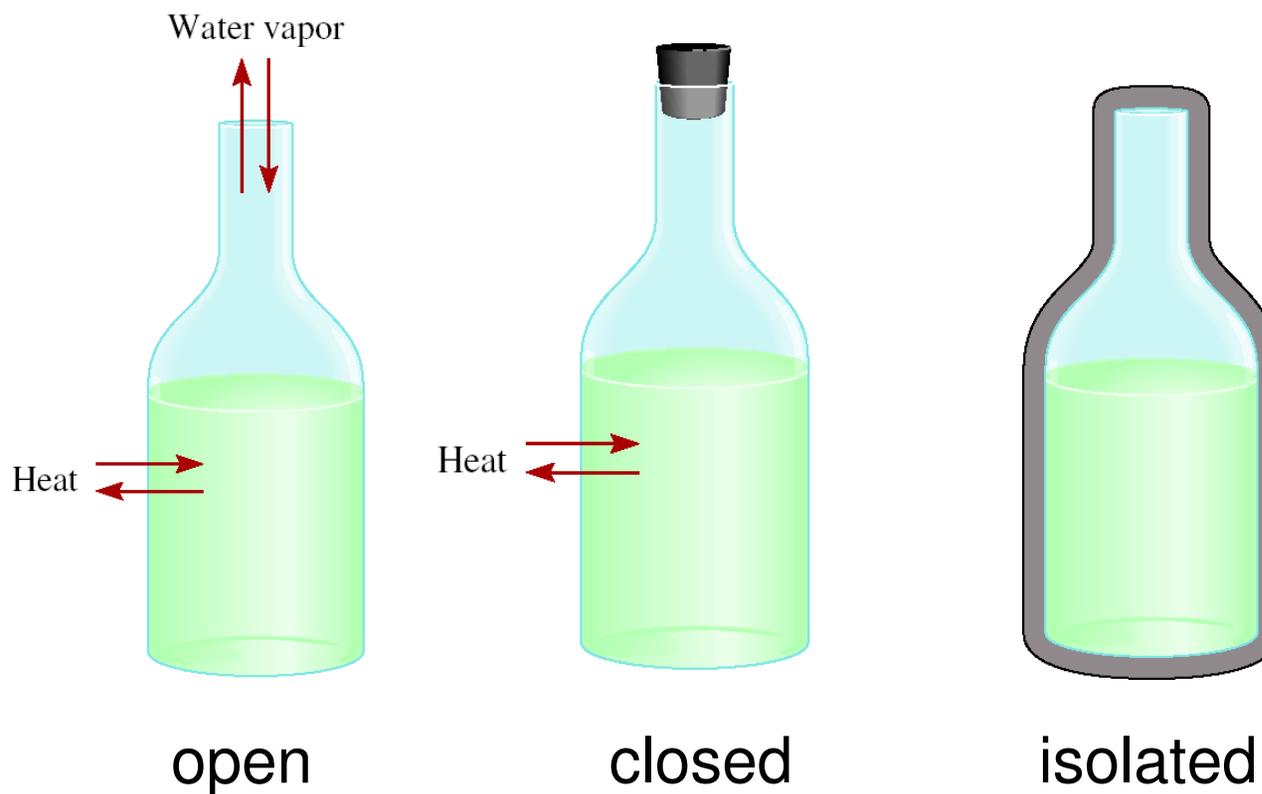
Temperature is a measure of the **thermal energy**.

Temperature ~~≠~~ Thermal Energy



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.

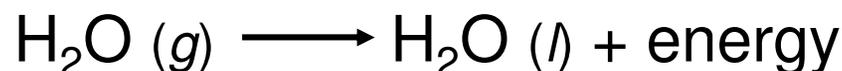


Exchange: mass & energy

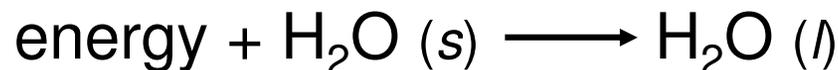
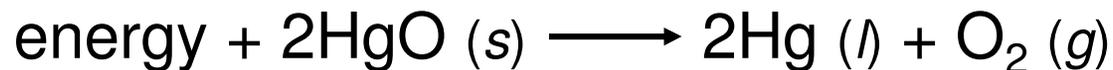
energy

nothing

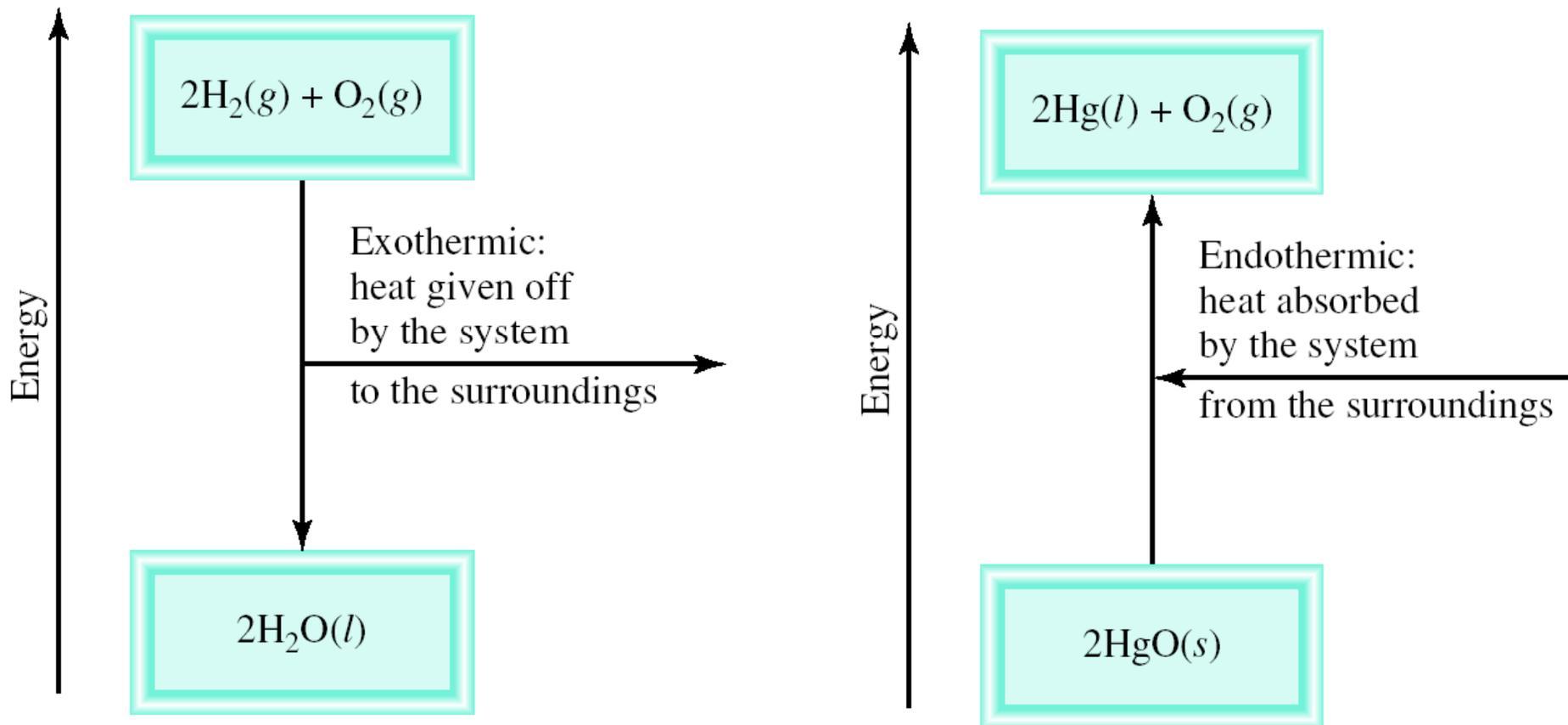
Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.



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



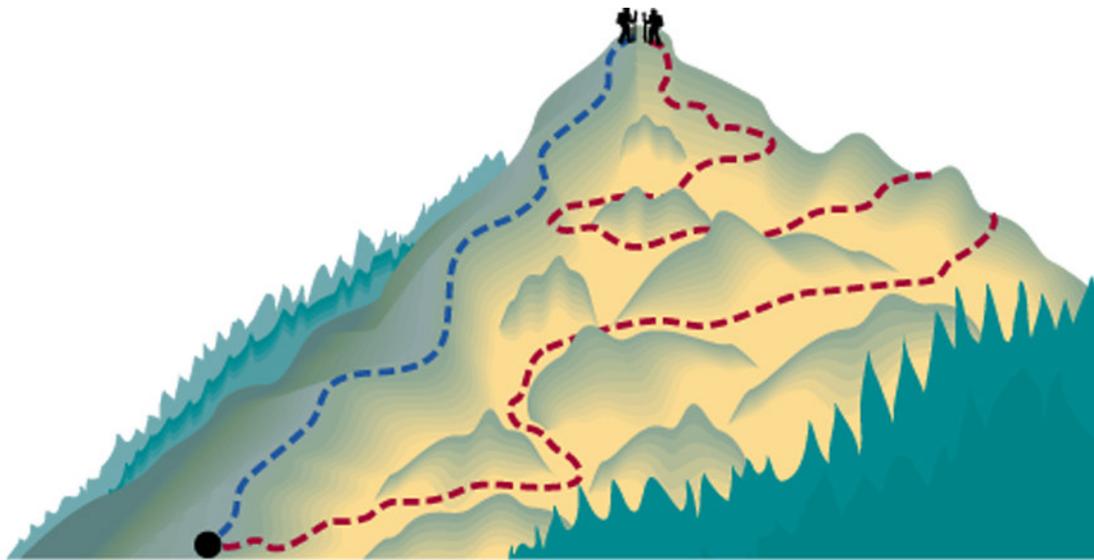
Schematic of Exothermic and Endothermic Processes



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

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

energy, pressure, volume, temperature



$$\Delta E = E_{final} - E_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

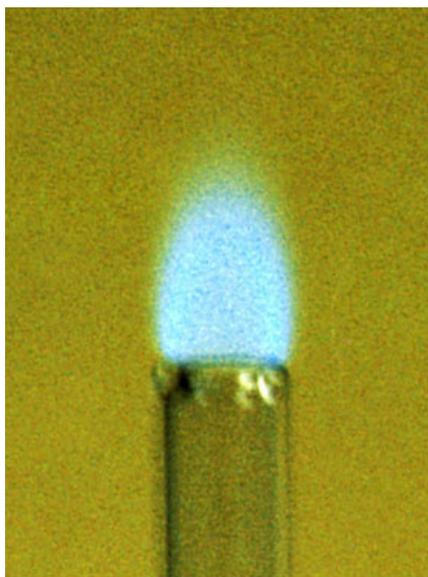
Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

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

$$w = F \times d$$

$$w = -P \Delta V$$

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

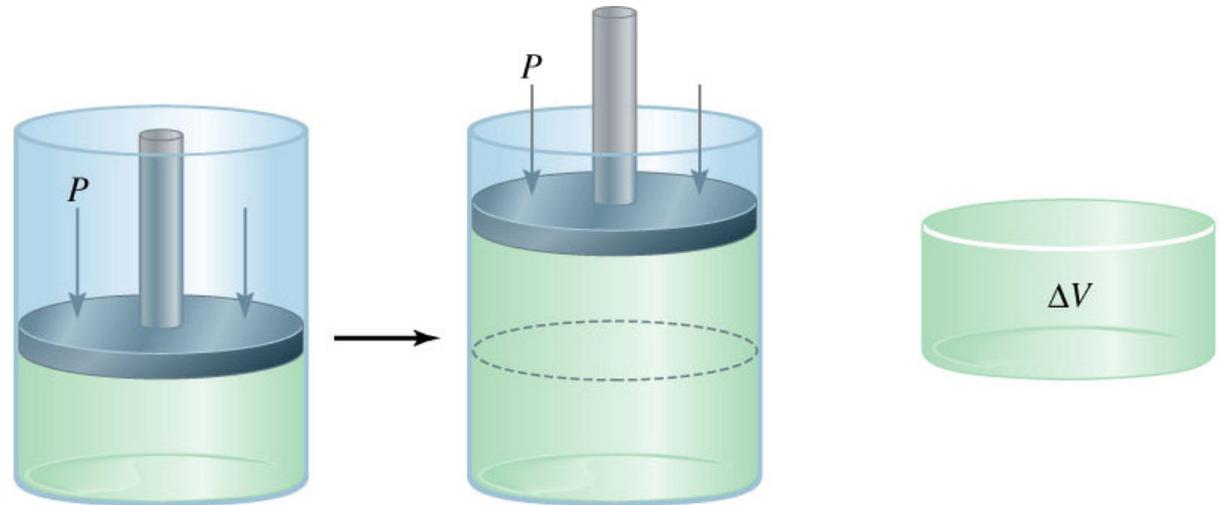
$$\Delta V > 0$$

$$-P\Delta V < 0$$

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

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?

$$w = -P \Delta V$$

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

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

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

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

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

Chemistry in Action: Making Snow

$$\Delta E = q + w$$

$$q = 0$$

$$w < 0, \Delta E < 0$$

$$\Delta E = C\Delta T$$

$$\Delta T < 0, \text{ SNOW!}$$



Enthalpy and the First Law of Thermodynamics

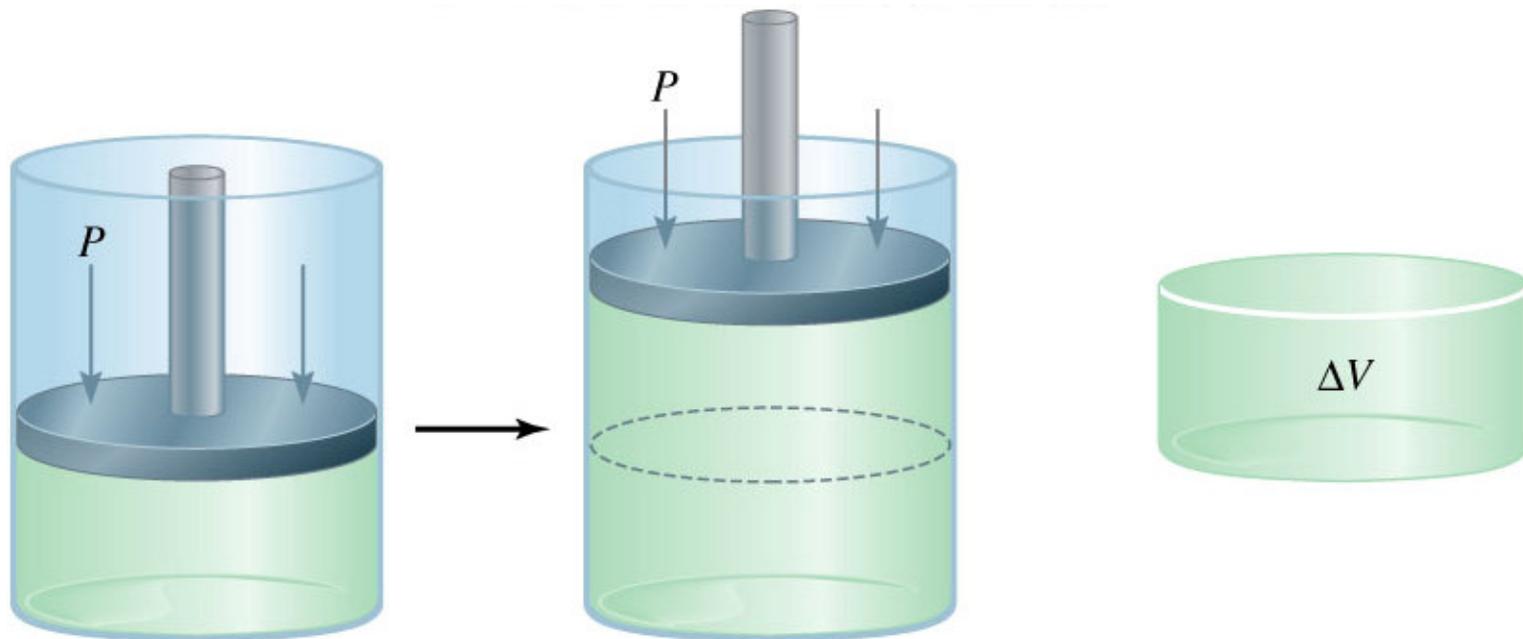
$$\Delta E = q + w$$

At constant pressure:

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

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

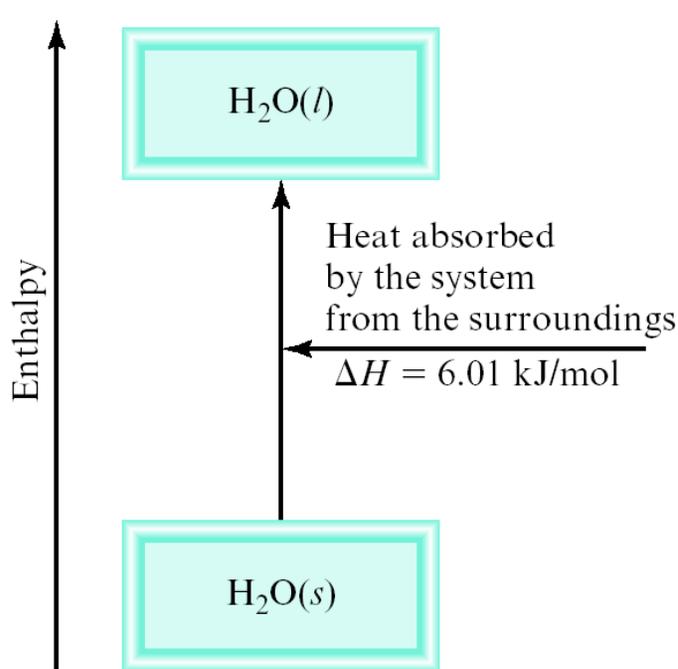
$$\Delta H = \Delta E + P\Delta V$$



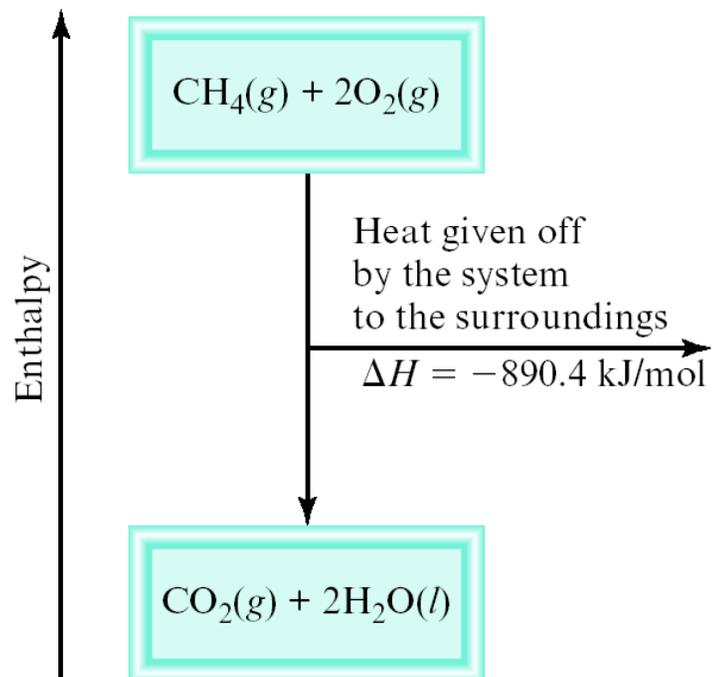
Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

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

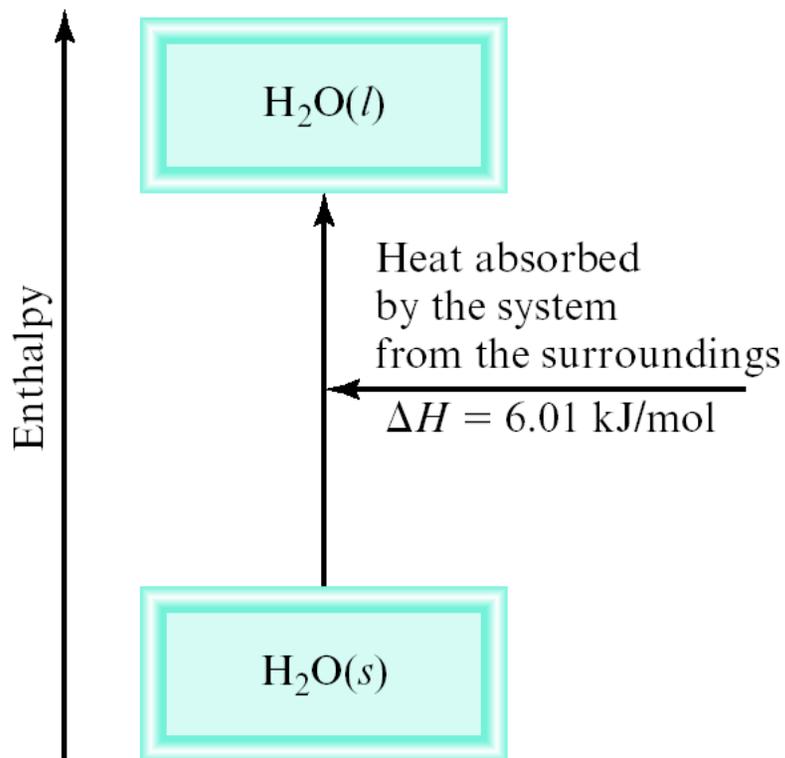


$$H_{\text{products}} < H_{\text{reactants}}$$
$$\Delta H < 0$$



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

Thermochemical Equations



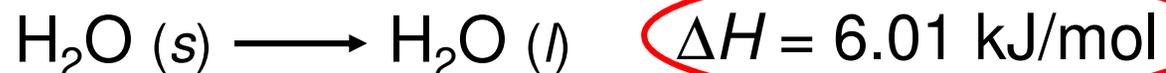
Is ΔH negative or positive?

System absorbs heat

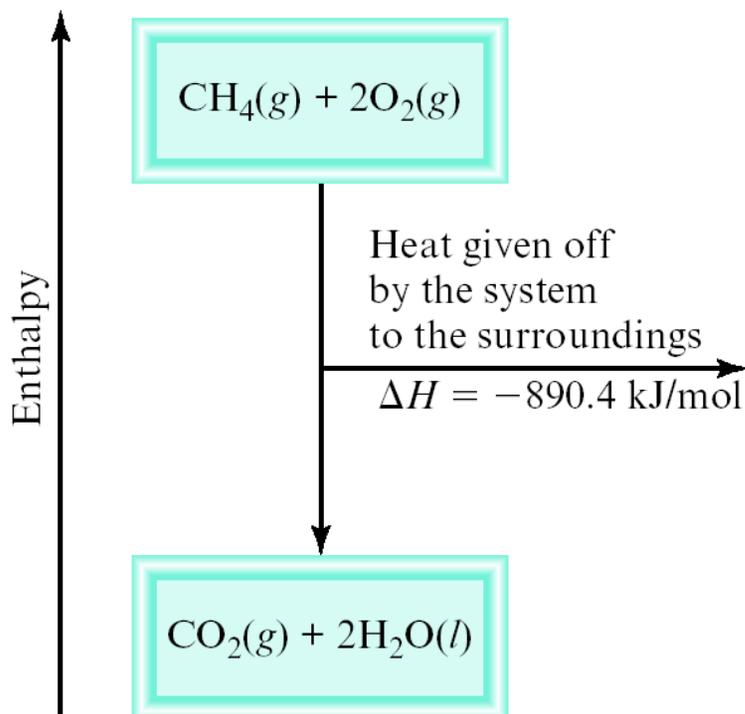
Endothermic

$\Delta H > 0$

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



Thermochemical Equations



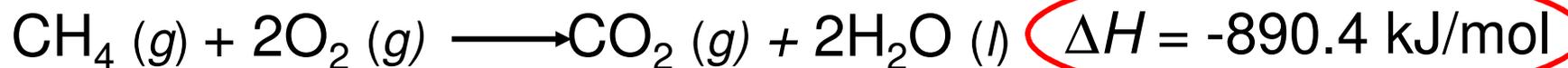
Is ΔH negative or positive?

System gives off heat

Exothermic

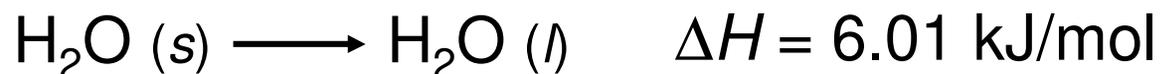
$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25⁰C 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?



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

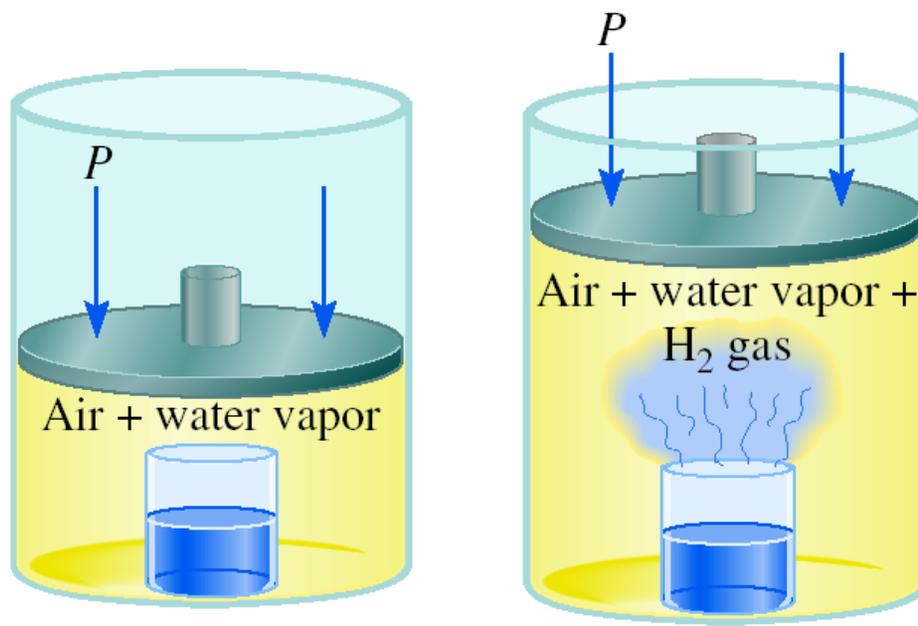
A Comparison of ΔH and ΔE



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

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

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



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?

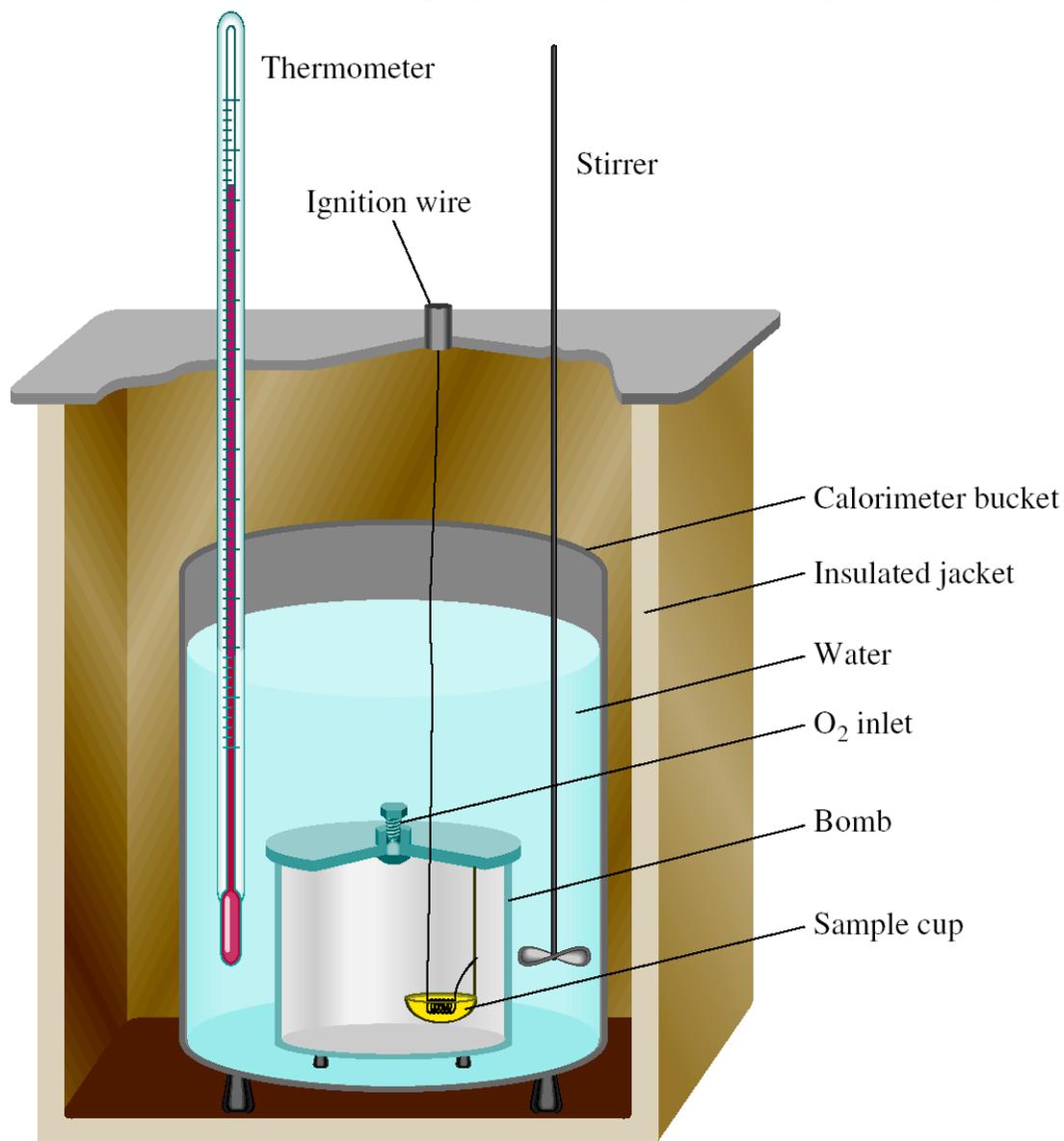
$$s \text{ of Fe} = 0.444 \text{ J/g} \cdot ^\circ\text{C}$$

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

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



Constant-Volume Calorimetry



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

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

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

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

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

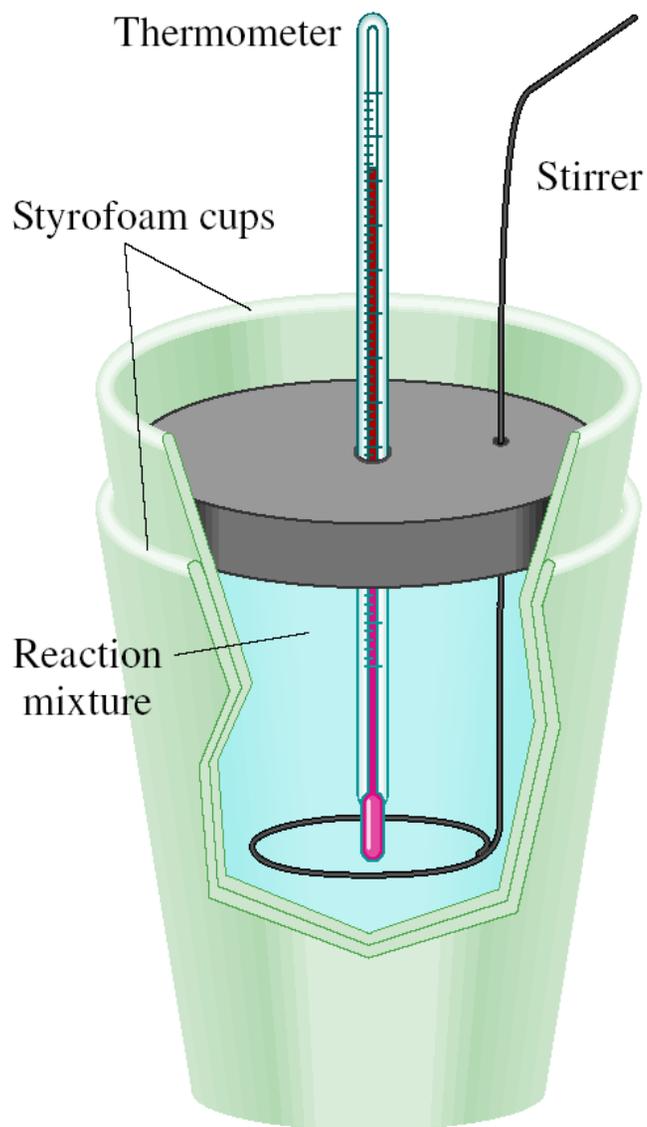
Reaction at Constant V

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

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

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 cal = 4.184 J

1 Cal = 1000 cal = 4184 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	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(<i>s</i>)	0	H ₂ O ₂ (<i>l</i>)	-187.6
AgCl(<i>s</i>)	-127.0	Hg(<i>l</i>)	0
Al(<i>s</i>)	0	I ₂ (<i>s</i>)	0
Al ₂ O ₃ (<i>s</i>)	-1669.8	HI(<i>g</i>)	25.9
Br ₂ (<i>l</i>)	0	Mg(<i>s</i>)	0
HBr(<i>g</i>)	-36.2	MgO(<i>s</i>)	-601.8
C(graphite)	0	MgCO ₃ (<i>s</i>)	-1112.9
C(diamond)	1.90	N ₂ (<i>g</i>)	0
CO(<i>g</i>)	-110.5	NH ₃ (<i>g</i>)	-46.3
CO ₂ (<i>g</i>)	-393.5	NO(<i>g</i>)	90.4
Ca(<i>s</i>)	0	NO ₂ (<i>g</i>)	33.85
CaO(<i>s</i>)	-635.6	N ₂ O(<i>g</i>)	81.56
CaCO ₃ (<i>s</i>)	-1206.9	N ₂ O ₄ (<i>g</i>)	9.66
Cl ₂ (<i>g</i>)	0	O(<i>g</i>)	249.4
HCl(<i>g</i>)	-92.3	O ₂ (<i>g</i>)	0
Cu(<i>s</i>)	0	O ₃ (<i>g</i>)	142.2
CuO(<i>s</i>)	-155.2	S(rhombic)	0
F ₂ (<i>g</i>)	0	S(monoclinic)	0.30
HF(<i>g</i>)	-271.6	SO ₂ (<i>g</i>)	-296.1
H(<i>g</i>)	218.2	SO ₃ (<i>g</i>)	-395.2
H ₂ (<i>g</i>)	0	H ₂ S(<i>g</i>)	-20.15
H ₂ O(<i>g</i>)	-241.8	Zn(<i>s</i>)	0
H ₂ O(<i>l</i>)	-285.8	ZnO(<i>s</i>)	-348.0

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

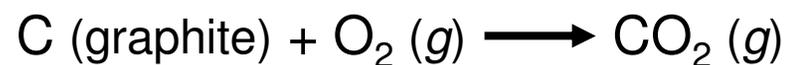
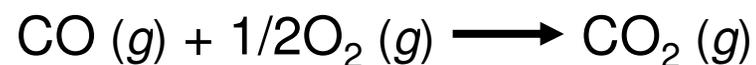
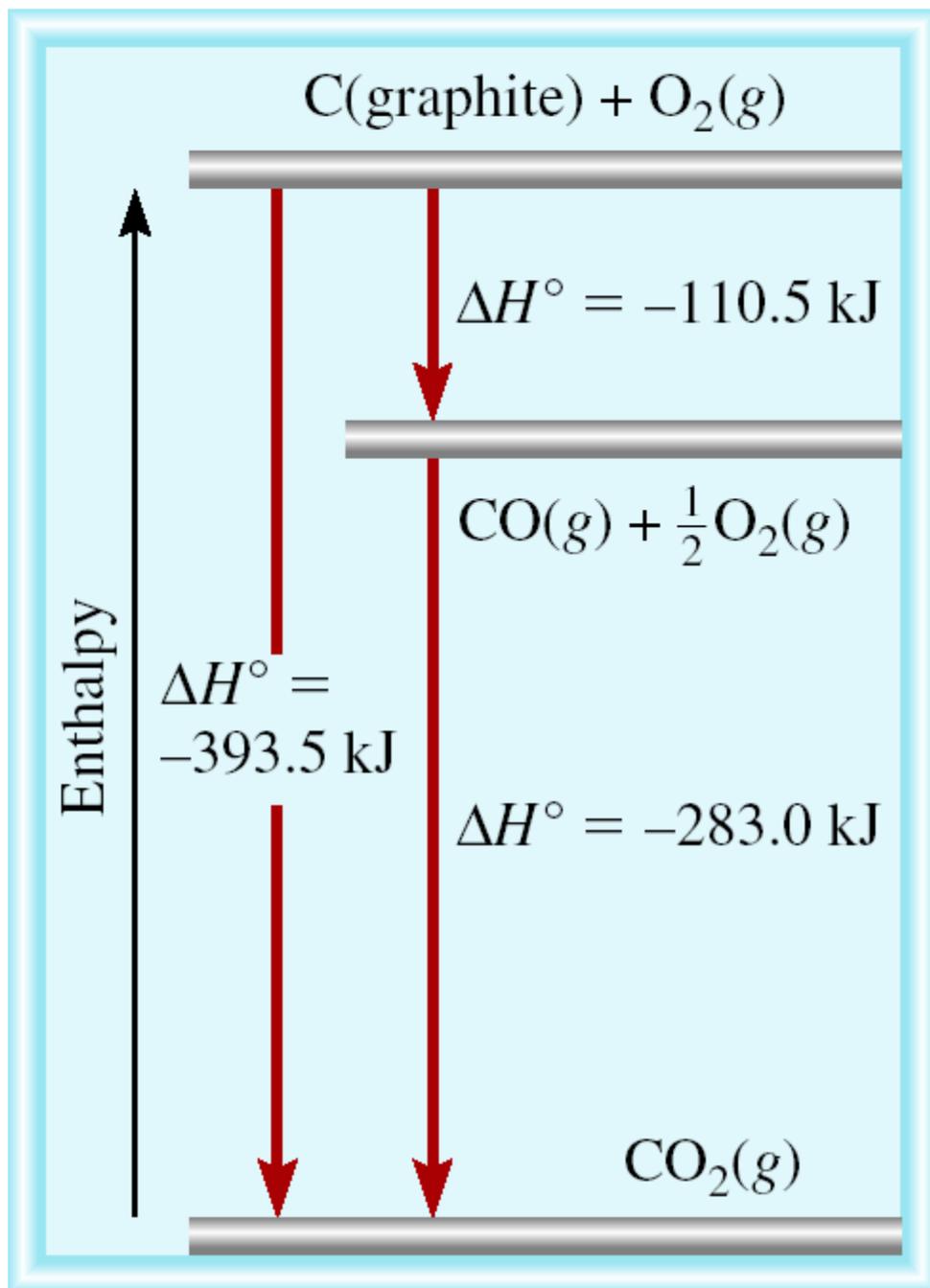


$$\Delta H_{\text{rxn}}^0 = [c\Delta H_{\text{f}}^0(\text{C}) + d\Delta H_{\text{f}}^0(\text{D})] - [a\Delta H_{\text{f}}^0(\text{A}) + b\Delta H_{\text{f}}^0(\text{B})]$$

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

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.)



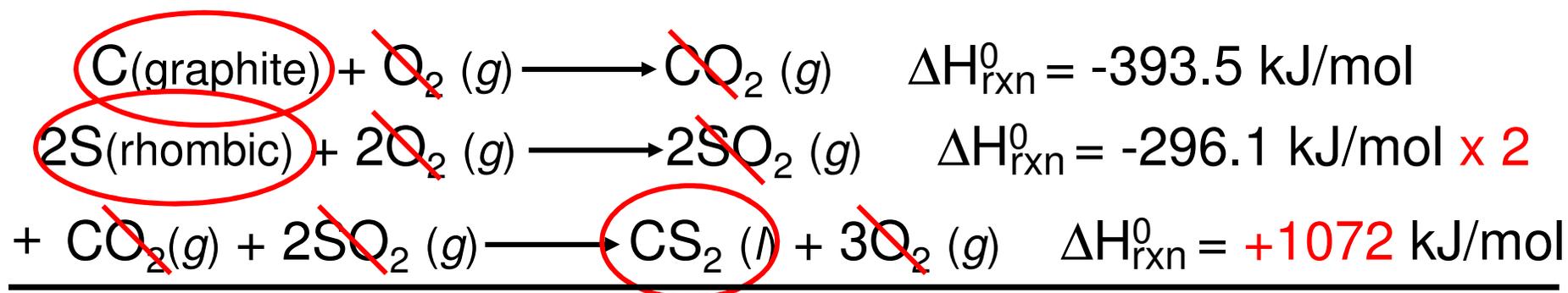
Calculate the standard enthalpy of formation of CS₂ (l) given that:



1. Write the enthalpy of formation reaction for CS₂

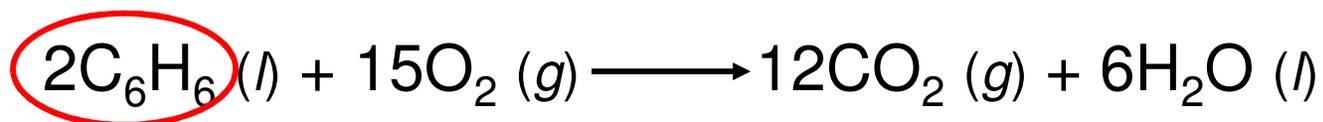


2. Add the given rxns so that the result is the desired rxn.



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

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.



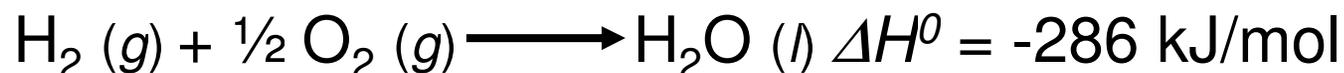
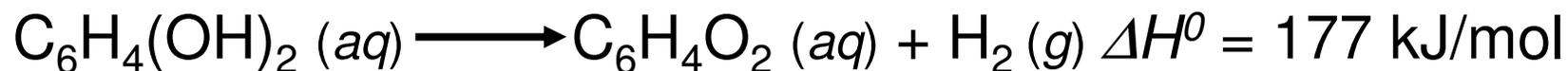
$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_{\text{f}}^0(\text{products}) - \sum m\Delta H_{\text{f}}^0(\text{reactants})$$

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

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

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

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

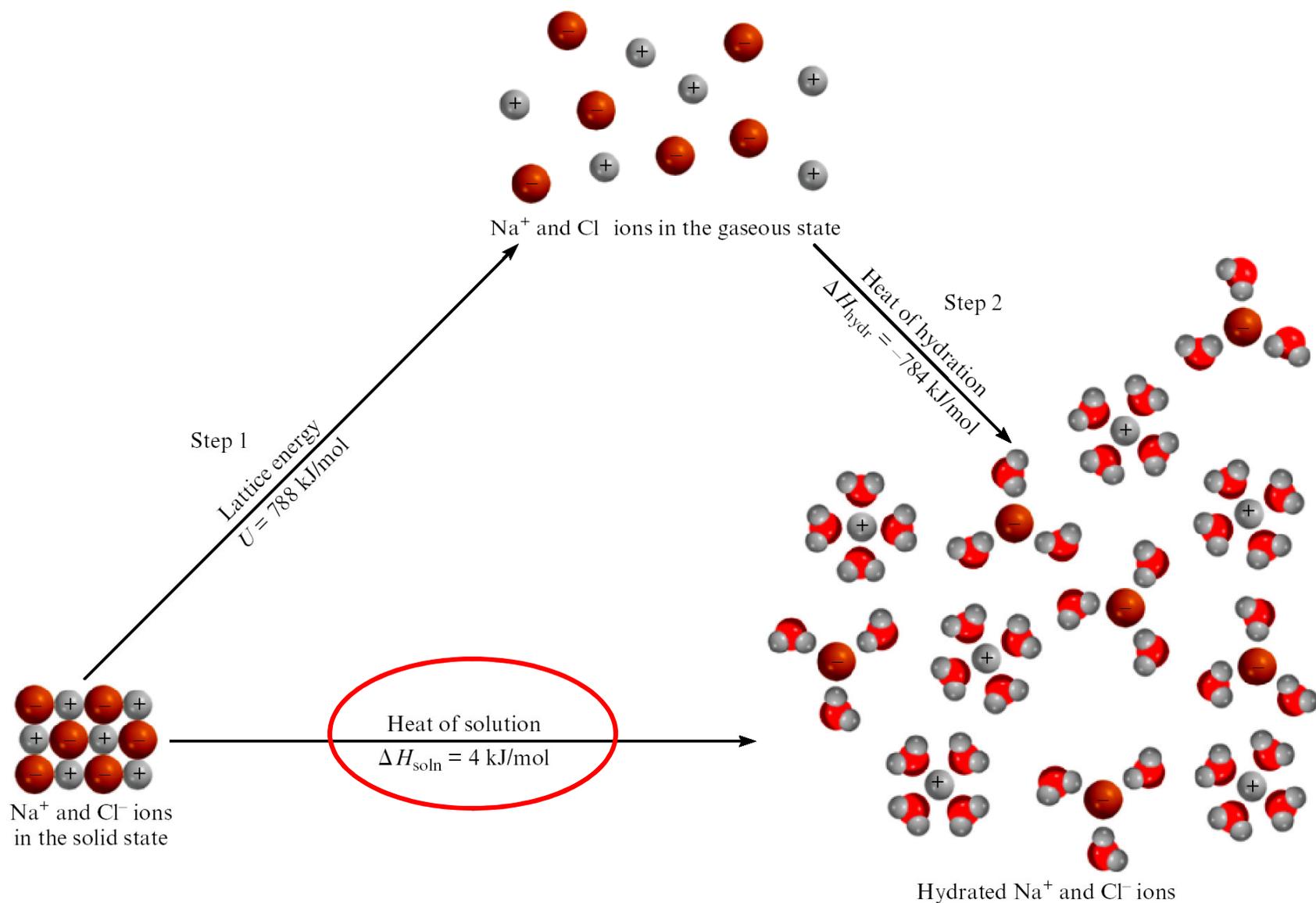
**Heats of Solution of
Some Ionic Compounds**

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



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