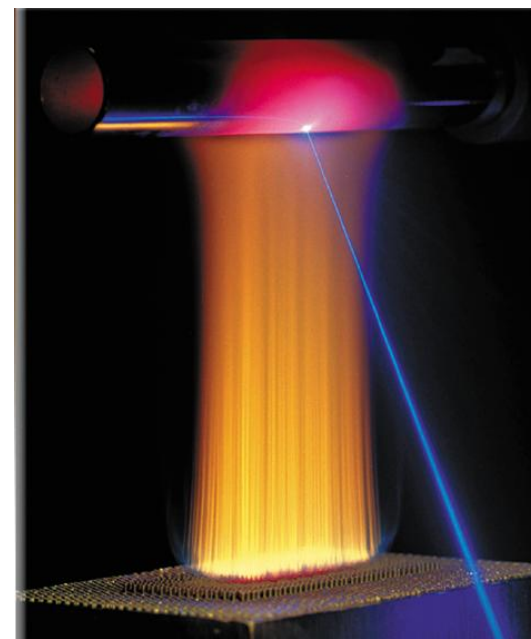




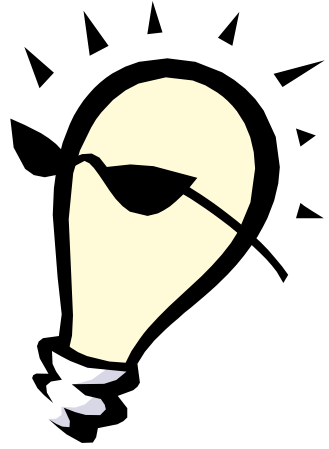
# Thermochemistry

## *Chapter 6*



**Energy** is the capacity to do work

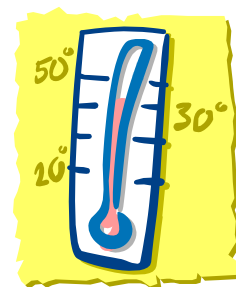
- **Radiant energy** comes from the sun and is earth's primary energy source
- **Thermal energy** is the energy associated with the random motion of atoms and molecules
- **Chemical energy** is the energy stored within the bonds of chemical substances
- **Nuclear energy** is the energy stored within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



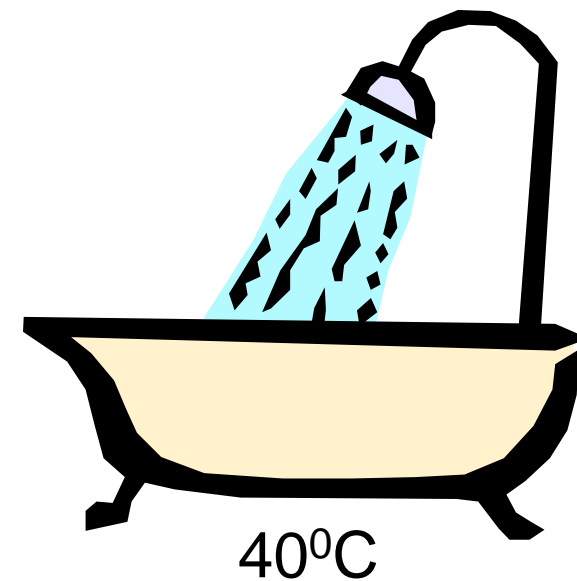
# Energy Changes in Chemical Reactions

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

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



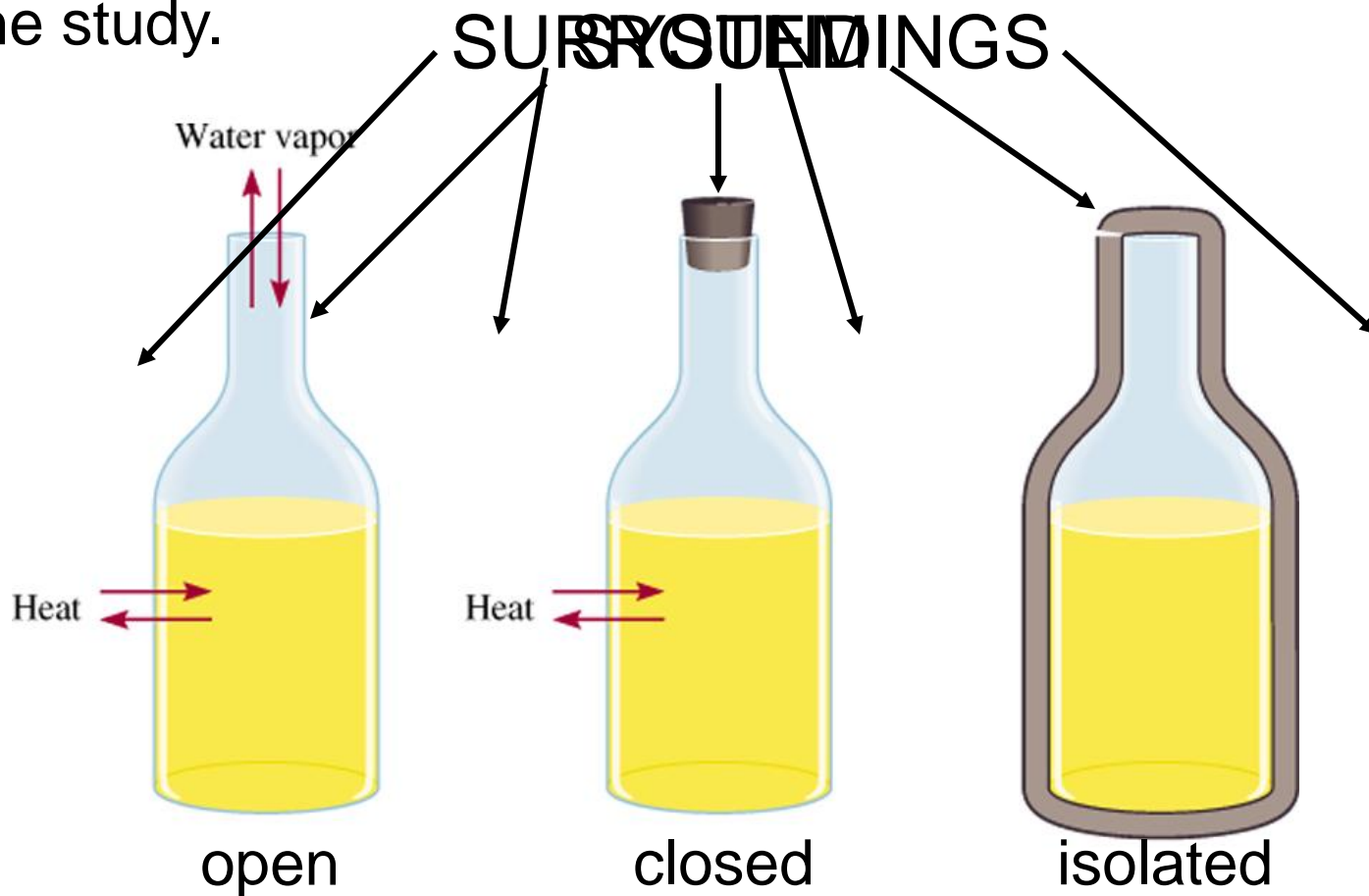
Temperature ~~X~~ Thermal Energy



greater 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.

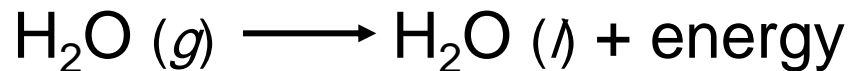
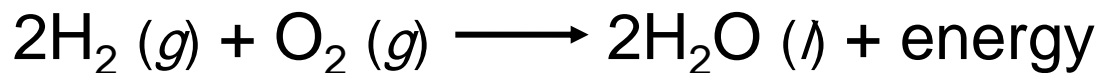


**Exchange:** mass & energy

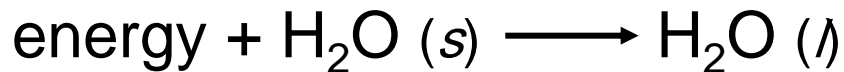
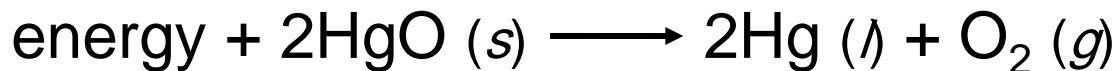
energy

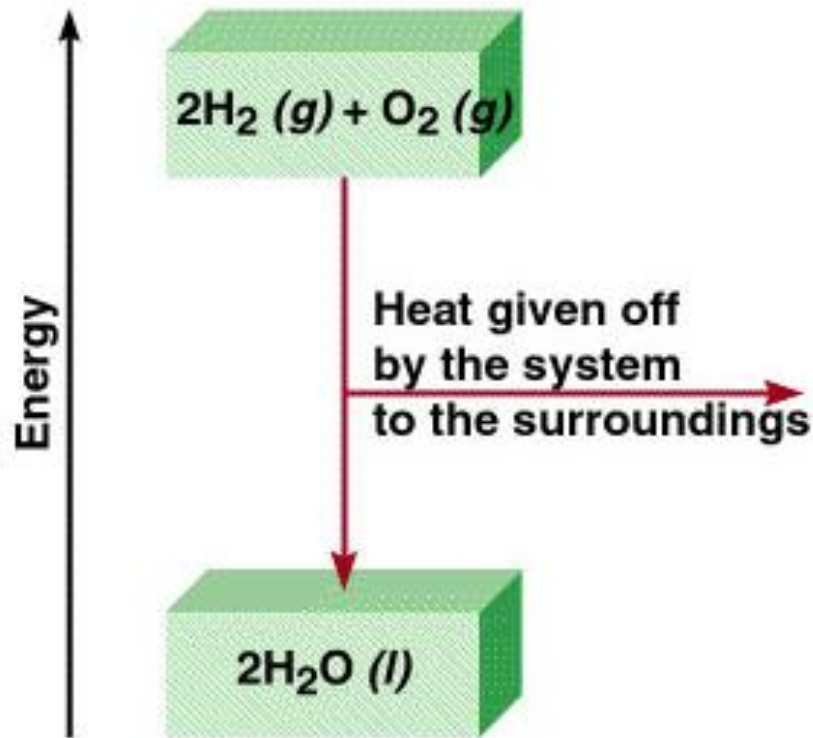
nothing

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

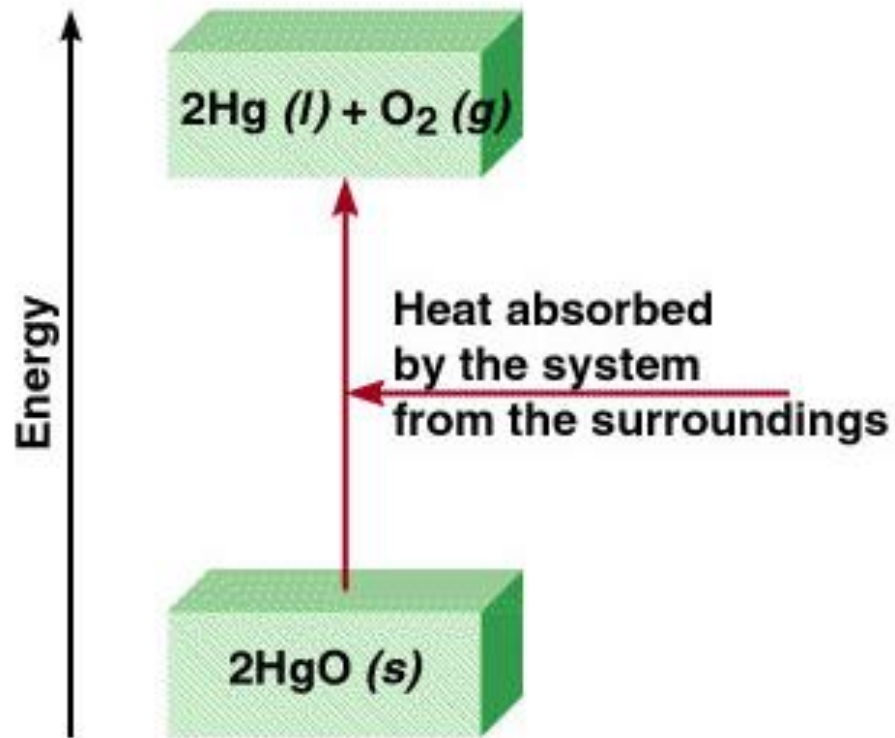


**Endothermic process** is any process in which heat has to be supplied to the system from the surroundings.





Exothermic

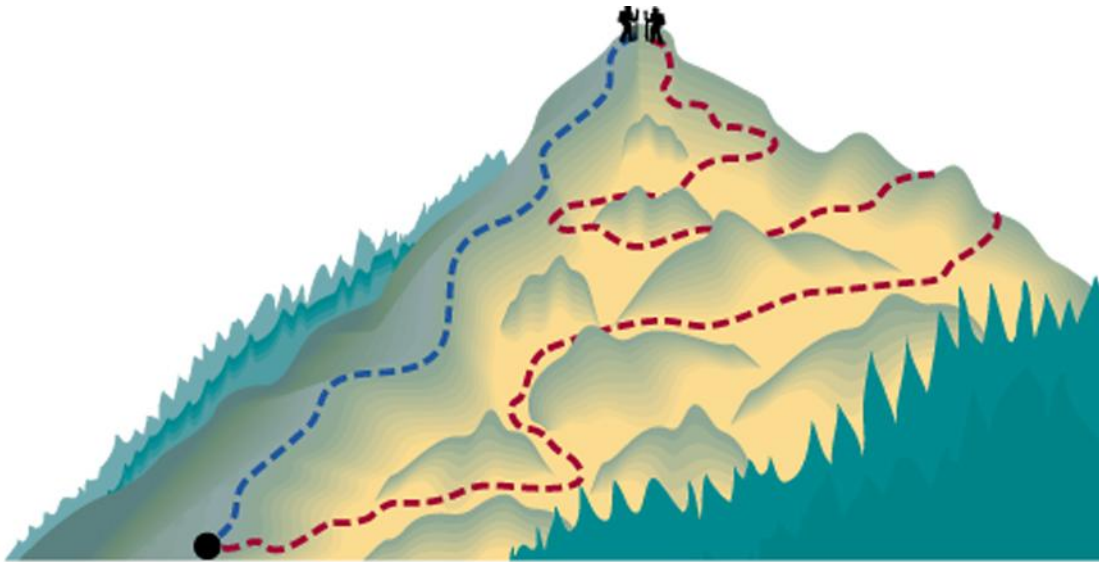


Endothermic

# Thermodynamics

***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.

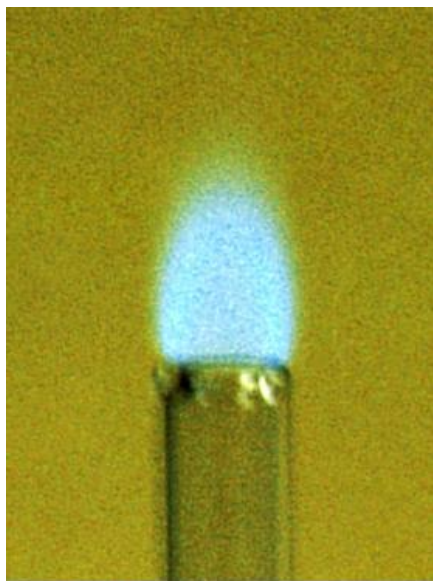


***First law of thermodynamics*** – energy can be converted from one form to another, but cannot be created or destroyed.

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

or

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



Exothermic chemical reaction!

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



Another form of the *first law* for  $\Delta E_{\text{system}}$

$$\Delta E = q + w$$

$\Delta E$  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**

<b>Process</b>	<b>Sign</b>
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

$$w = Fd$$

$$w = -P \Delta V$$

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

$$\Delta V > 0$$

$$-P\Delta V < 0$$

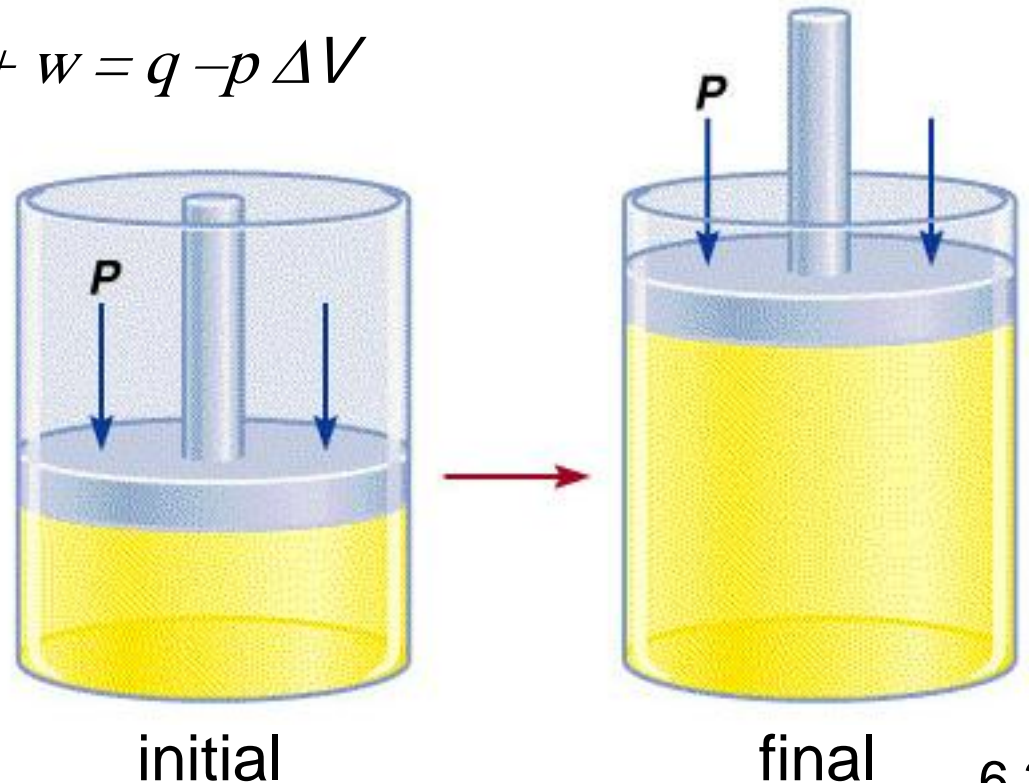
$$W_{\text{sys}} < 0$$

$$\Delta E = q + w = q - p \Delta V$$



Work is  
not a  
state  
function!

$$\Delta W \neq W_{\text{final}} - W_{\text{initial}}$$





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

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

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

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

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

# 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

$$\Delta E = q + w \text{ At Constant Temperature}$$

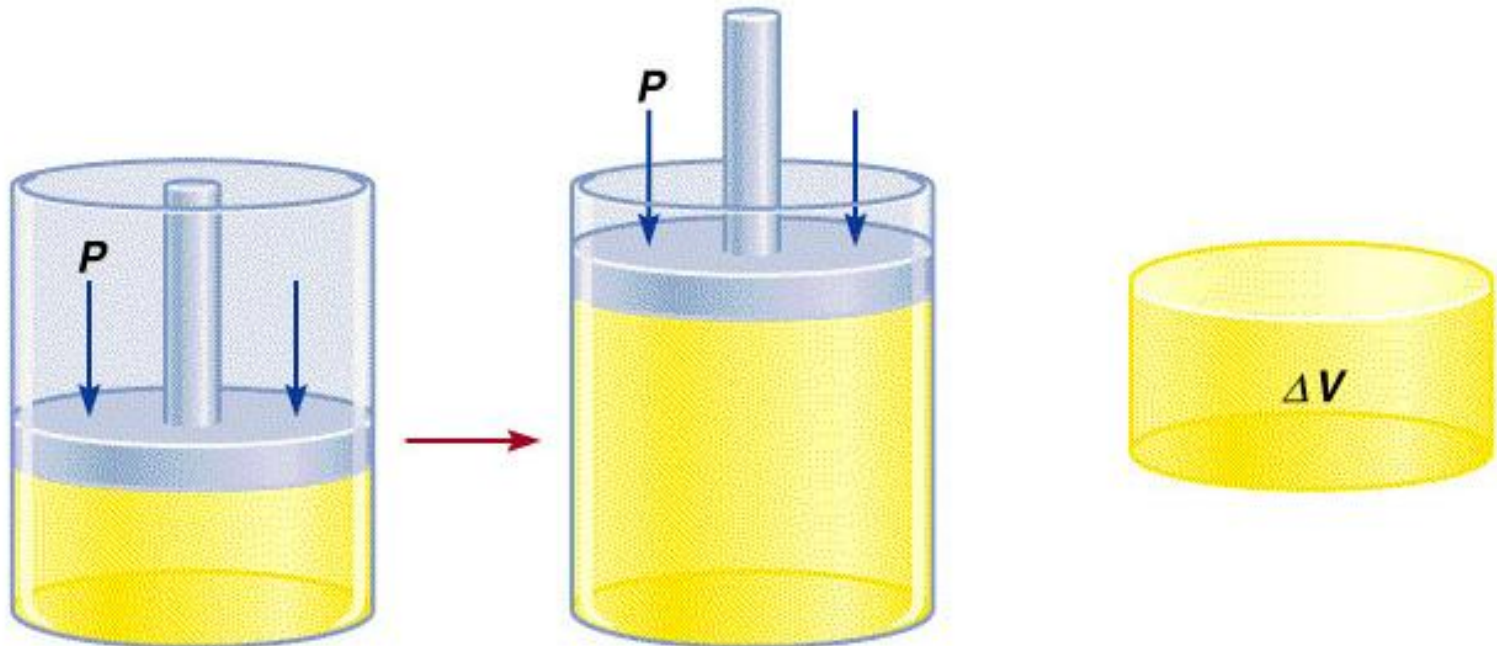


At constant pressure:

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

$$\Delta E = \Delta H - P\Delta V \text{ At Constant Pressure}$$

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

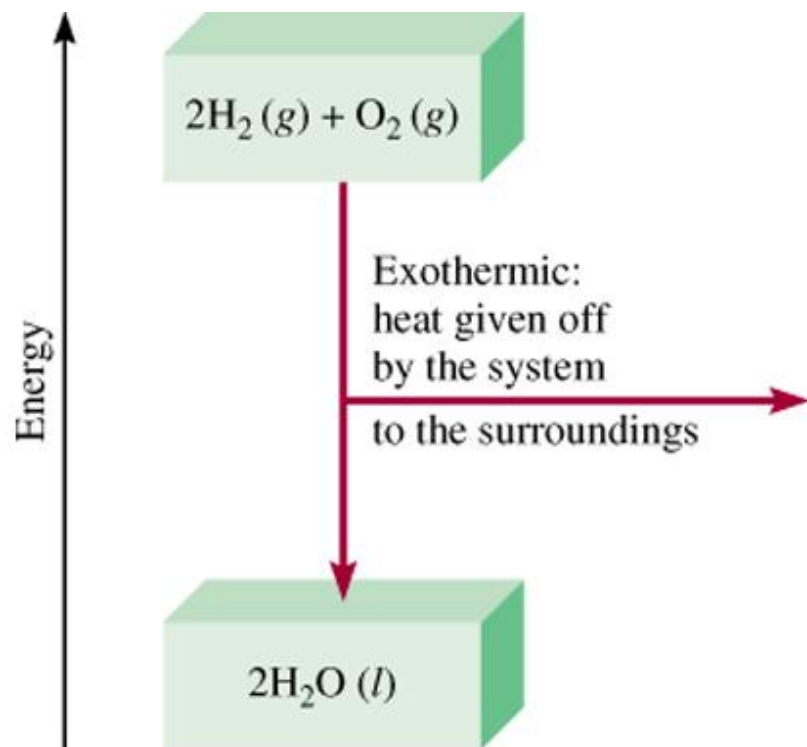




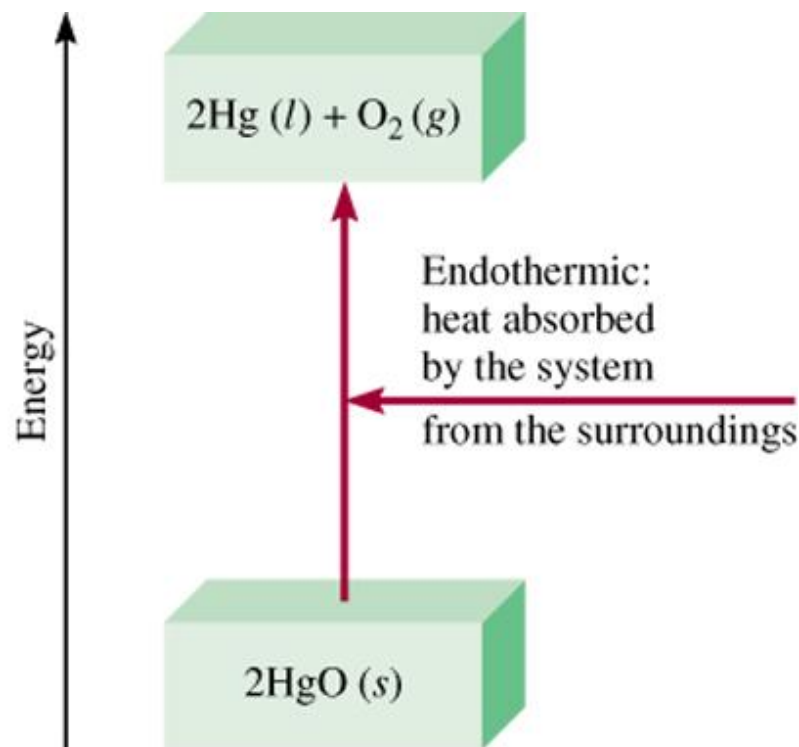
**Enthalpy ( $H$ )** is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

$\Delta H$  = heat given off or absorbed during a reaction **at constant pressure**

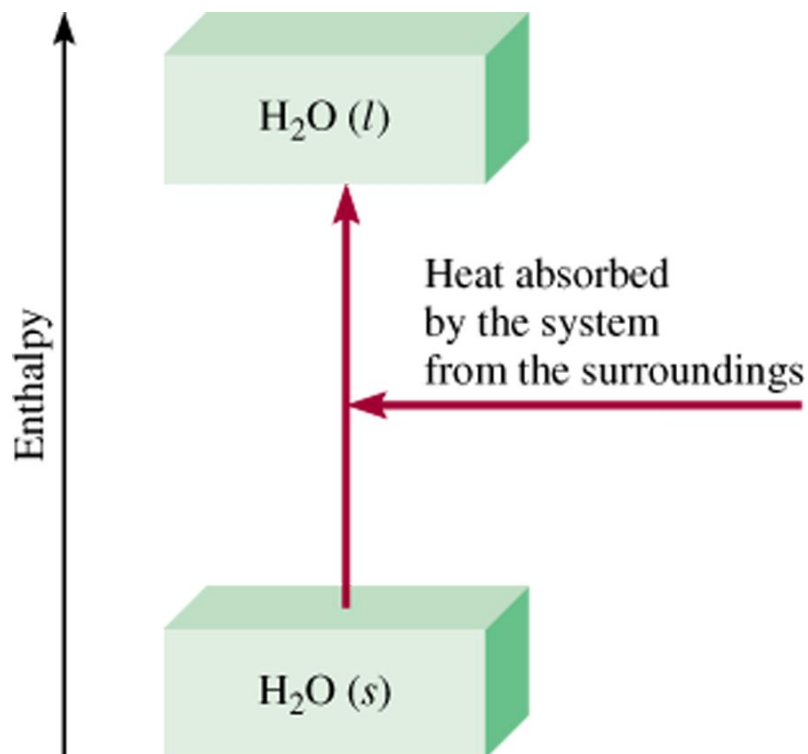


$$H_{\text{products}} < H_{\text{reactants}}$$
$$\Delta H < 0$$



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

# Thermochemical Equations



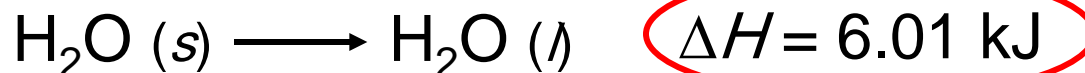
Is  $\Delta H$  negative or positive?

System absorbs heat

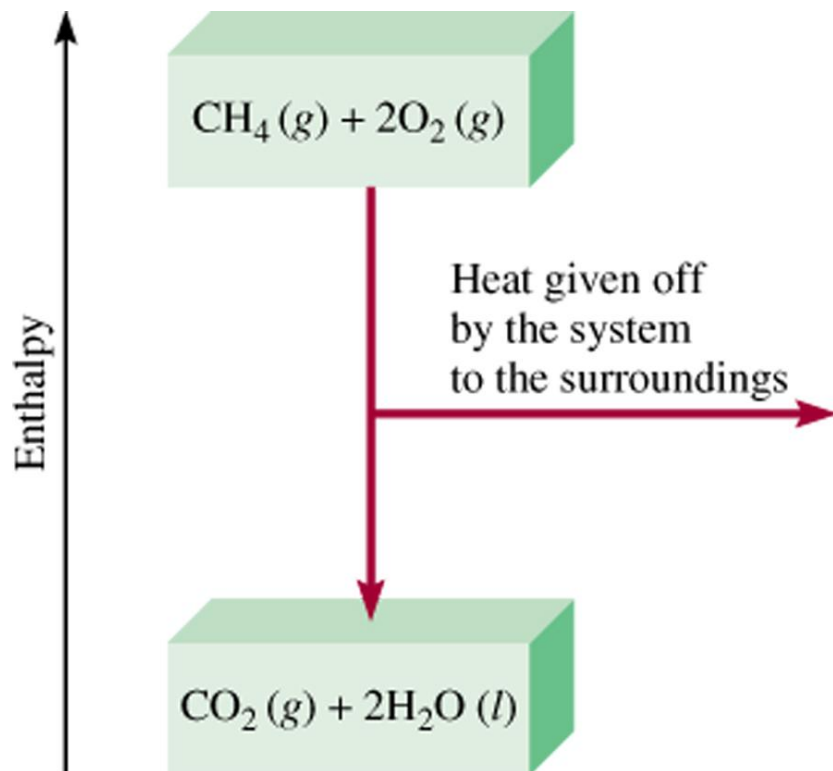
Endothermic

$$\Delta H > 0$$

6.01 kJ are absorbed for every 1 mole of ice that melts at  $0^\circ\text{C}$  and 1 atm.



# Thermochemical Equations



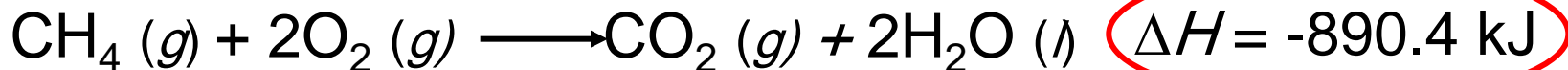
Is  $\Delta H$  negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

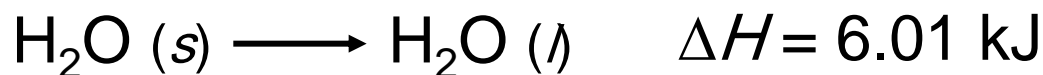
890.4 kJ are released for every 1 mole of methane that is combusted at 25<sup>0</sup>C and 1 atm.





# Thermochemical Equations

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



- If you reverse a reaction, the sign of  $\Delta H$  changes



- If you multiply both sides of the equation by a factor  $n$ , then  $\Delta H$  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 ( $\text{P}_4$ ) burn in air?

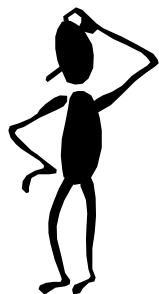


$$n = m (\text{g}) / \text{molar mass} (\text{g/mol}) = 266 \text{ g} / 123.9 (\text{g/mol})$$

$$1 \text{ mol} \longrightarrow 3013$$

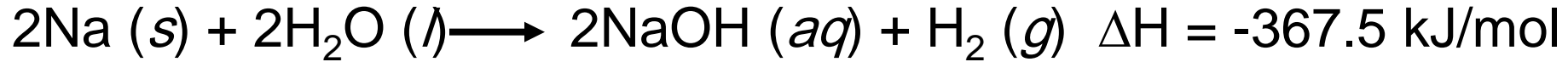
$$2.15 \text{ mol} \longrightarrow x$$

$$2.15 \text{ mol} \times 3013 \text{ kJ} / 1 \text{ mol} = 6470 \text{ kJ}$$



# A Comparison of $\Delta H$ and $\Delta E$

Find  $\Delta E$  for the reaction:

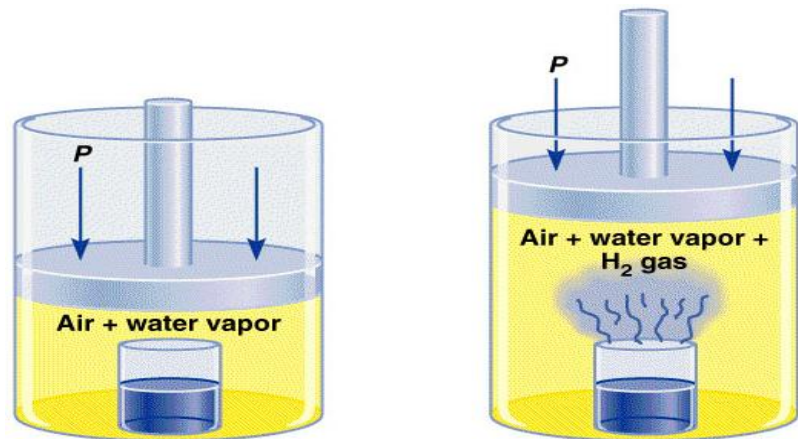


$$\Delta E = \Delta H - P\Delta V \quad \text{At } 25^\circ\text{C, 1 mole H}_2 = 24.5 \text{ L at 1 atm}$$

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

$$= 1 \text{ atm} \times 24.5 \text{ L} \times 101.3 / 1000 = 2.5 \text{ kJ}$$

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



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**.

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 <sub>2</sub> O	4.184
C <sub>2</sub> H <sub>5</sub> OH (ethanol)	2.46

TABLE 6.2

$$C = ms$$

Heat ( $q$ ) absorbed or released:

$$q = ms\Delta t$$

$$q = C\Delta t$$

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



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

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

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

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

Find the final temperature when 34000 j of heat evolved (given off) on cooling 869 g of Iron bar at 94 °C?

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

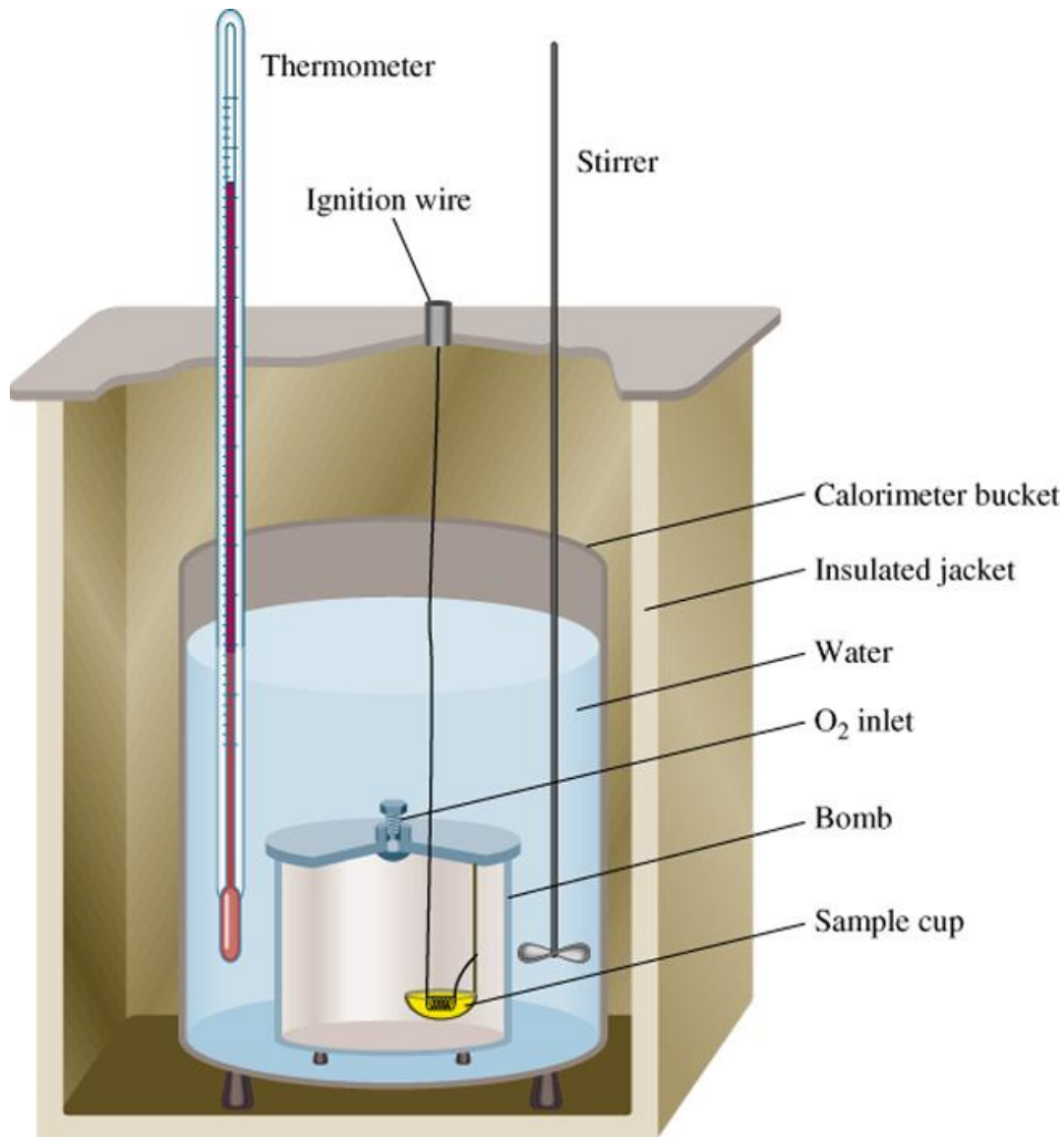
$$q = ms\Delta T$$

$$-34000 = 869 \text{ g} \times 0.444 \text{ J/g} \cdot ^\circ\text{C} \times \Delta T$$

$$\Delta T = -34000 / 869 \times 0.444 = -89^\circ\text{C}$$

$$T_f = T_i + \Delta T = 94 - 89 = 5^\circ\text{C}$$

# Constant-Volume Calorimetry



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

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

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

$$q_{\text{water}} = ms\Delta t$$

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

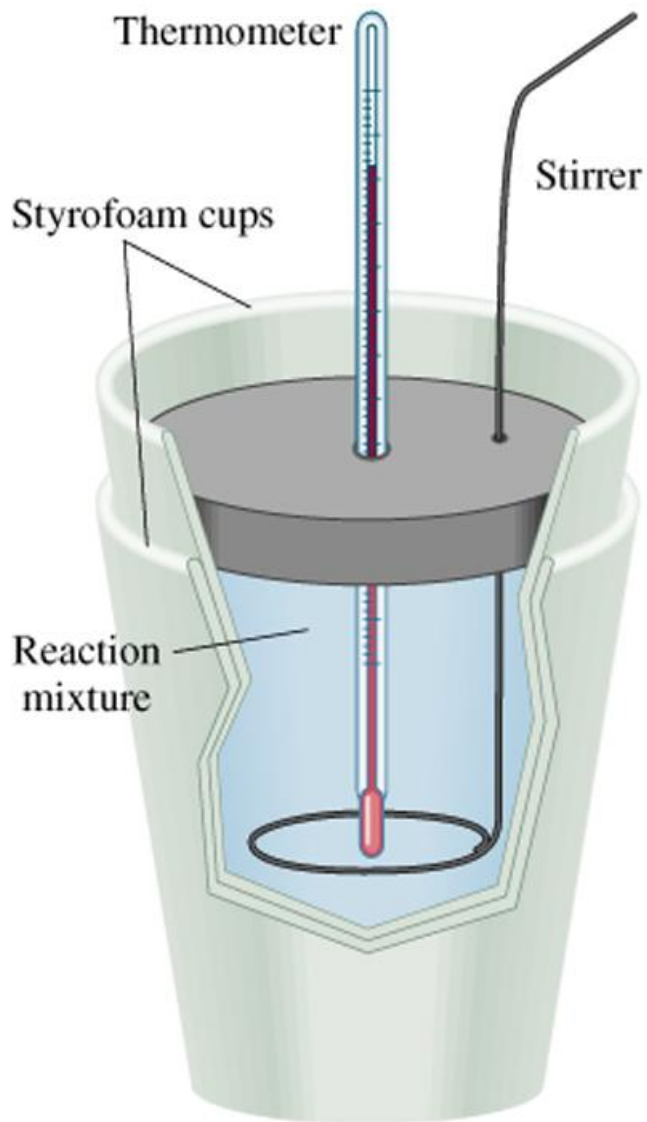
Reaction at Constant  $V$

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

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

No heat enters or leaves!

# Constant-Pressure Calorimetry



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

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

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

$$q_{\text{water}} = ms\Delta t$$

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

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

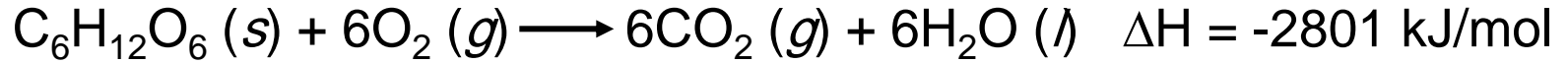
Type of Reaction	Example	$\Delta H$ (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	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

<b>Nutrition Facts</b>	
Serving Size 6 cookies (28g)	
Servings Per Container about 11	
<b>Amount Per Serving</b>	
<b>Calories</b> 120	Calories from Fat 30
<b>% Daily Value*</b>	
<b>Total Fat</b> 4g	<b>6%</b>
Saturated Fat 0.5g	<b>4%</b>
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
<b>Cholesterol</b> 5mg	<b>2%</b>
<b>Sodium</b> 105mg	<b>4%</b>
<b>Total Carbohydrate</b> 20g	<b>7%</b>
Dietary Fiber Less than 1gram	<b>2%</b>
Sugars 7g	
<b>Protein</b> 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** ( $\Delta H_f^0$ ) as a reference point for all enthalpy expressions.

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

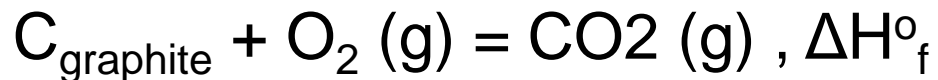
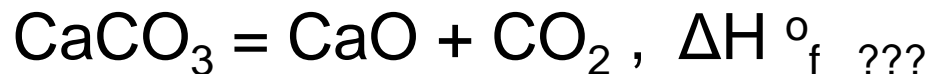
The standard enthalpy of formation of any element in its most stable form is zero.

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

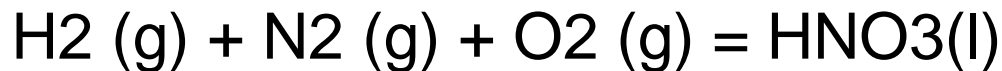
$$\Delta H_f^0 (\text{C, graphite}) = 0$$

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

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



Which of the following reactions represent heat of formation of nitric acid HNO<sub>3</sub> ?



The **standard enthalpy of reaction** ( $\Delta H_{\text{rxn}}^0$ ) is the enthalpy of a reaction carried out at 1 atm.



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

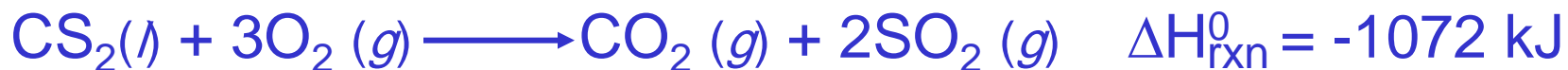
$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_{\text{f}}^0(\text{products}) - \sum m\Delta H_{\text{f}}^0(\text{reactants})$$

***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.

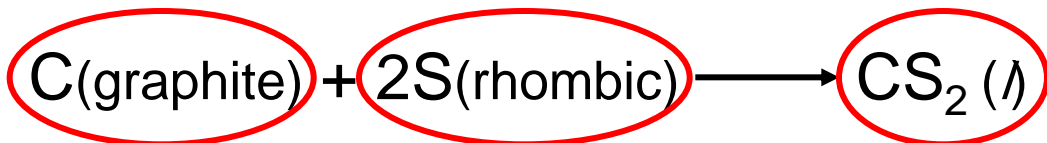
(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)



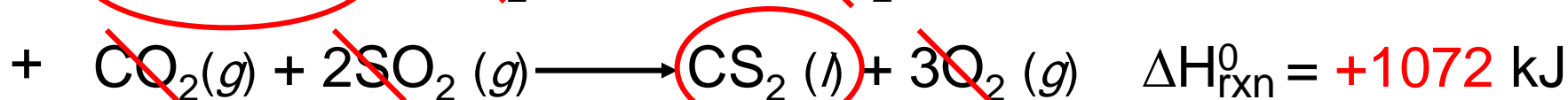
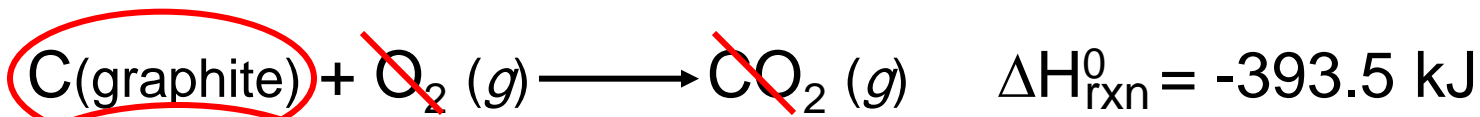
Calculate the standard enthalpy of formation of  $\text{CS}_2(l)$  given that:



1. Write the enthalpy of formation reaction for  $\text{CS}_2$



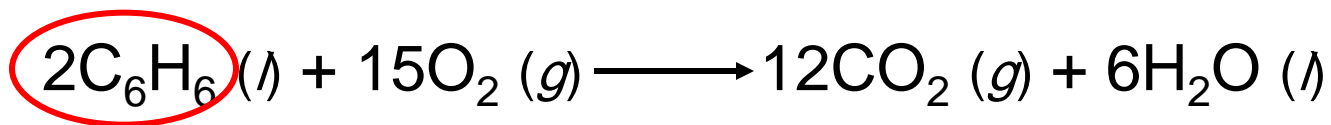
2. Add the given rxns so that the result is the desired rxn.



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



Benzene ( $C_6H_6$ ) 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.



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

$$\Delta H_{rxn}^0 = [12\Delta H_f^0 (CO_2) + 6\Delta H_f^0 (H_2O)] - [2\Delta H_f^0 (C_6H_6)]$$

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

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

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

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

**Heats of Solution of  
Some Ionic Compounds**

<b>Compound</b>	<b><math>\Delta H_{\text{soln}}</math> (kJ/mol)</b>
LiCl	-37.1
CaCl <sub>2</sub>	-82.8
NaCl	4.0
KCl	17.2
NH <sub>4</sub> Cl	15.2
NH <sub>4</sub> NO <sub>3</sub>	26.2

**TABLE 6.5**

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

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

# The Solution Process for NaCl

