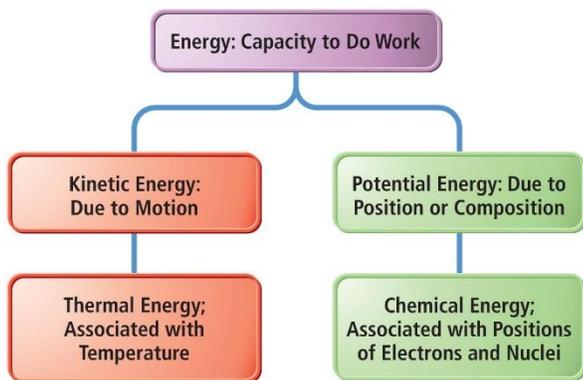


THERMOCHEMISTRY & DEFINITIONS

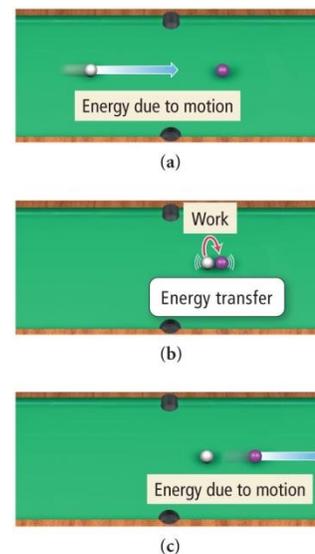
- Thermochemistry is the study of the study of relationships between chemistry and energy.
- All chemical changes and many physical changes involve exchange of energy with the surroundings. In this chapter we will study the relationships between chemical reactions and energy, and how they can be quantified.

Nature of Energy:

- **Energy** is the capacity to do work, and **work** is defined as force acting through a distance.
- There are many types of energy. Among them are kinetic (moving), potential (stored), thermal energy and chemical energy.
- The law of conservation of energy states that energy can be neither created, nor destroyed. However, energy can be transformed from one object to another through work.



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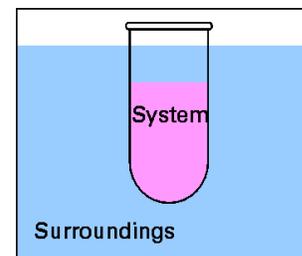


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THERMOCHEMISTRY & DEFINITIONS

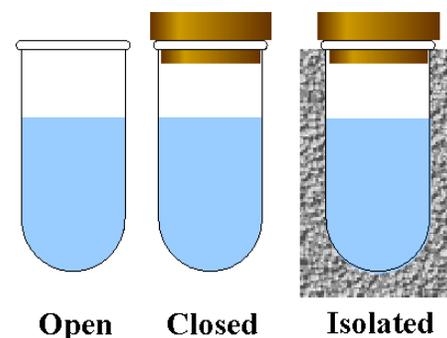
System and Surroundings:

- **System** is defined as the part of the universe we happen to be studying. For example, the system can be the chemicals in a beaker undergoing a change.
- **Surrounding** is defined as everything outside the system with which it can exchange energy. For example, in the example above, the surroundings could be the solution the chemicals are dissolved in, the air in the room, etc.



Three types of systems can be present:

- **Open:** exchange of energy and matter
- **Closed:** exchange of energy but not matter
- **Isolated:** No exchange of energy or matter



Units of Energy:

- The SI units of energy are **joules (J)** which is defined as $1 \text{ kgm}^2/\text{s}^2$.
- Another commonly used units of energy is **calorie (cal)**, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C .
- Home energy costs are usually based on another very large unit of energy, **kilowatt-hour (kWh)**.
- The conversion factors between all the units of energy are shown below:

$$\text{KE} = \frac{1}{2}mv^2$$

↑ kg ↑ m/s

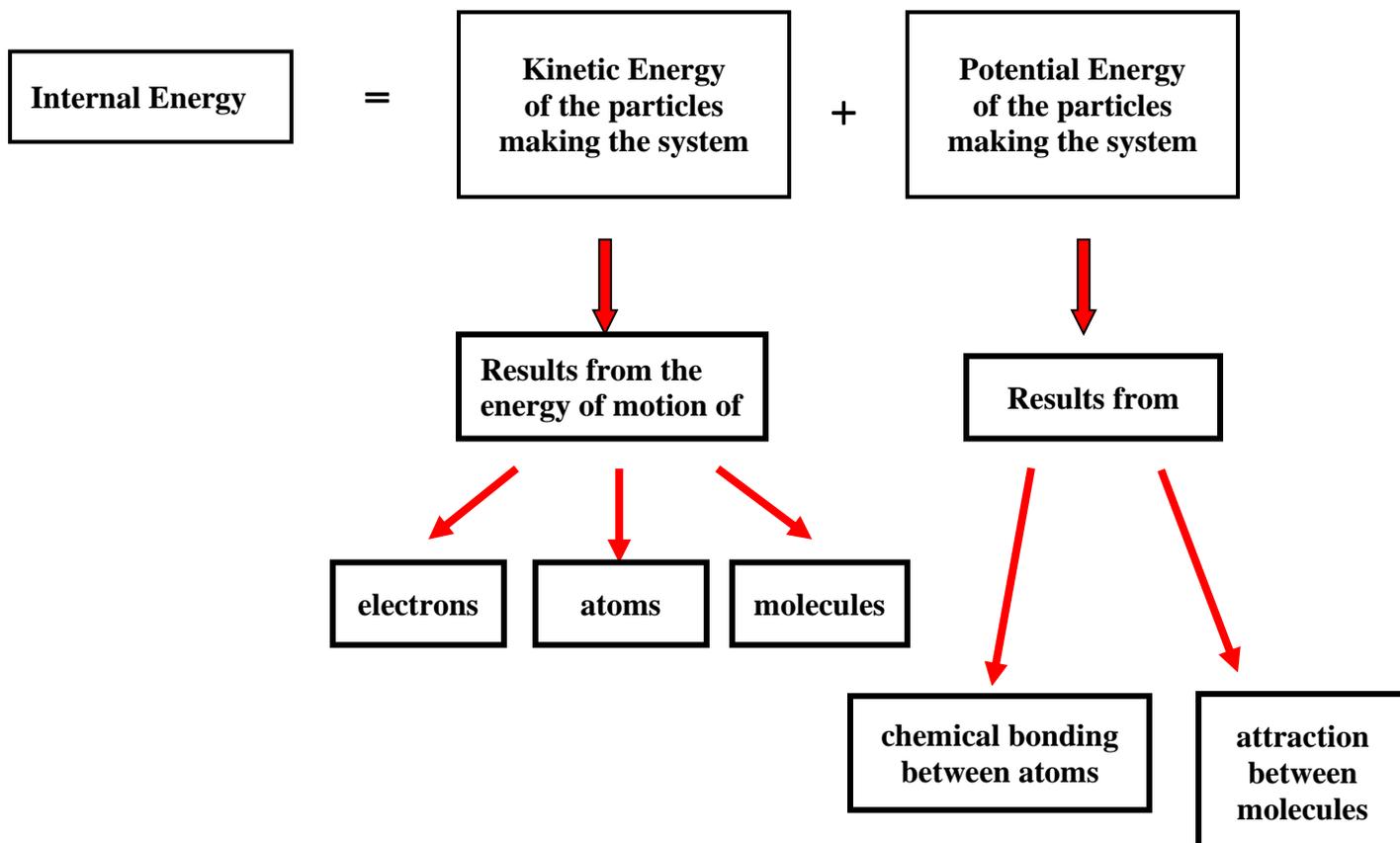
TABLE 6.1 Energy Conversion Factors*

1 calorie (cal)	= 4.184 joules (J)
1 Calorie (Cal) or kilocalorie (kcal)	= 1000 cal = 4184 J
1 kilowatt-hour (kWh)	= $3.60 \times 10^6 \text{ J}$

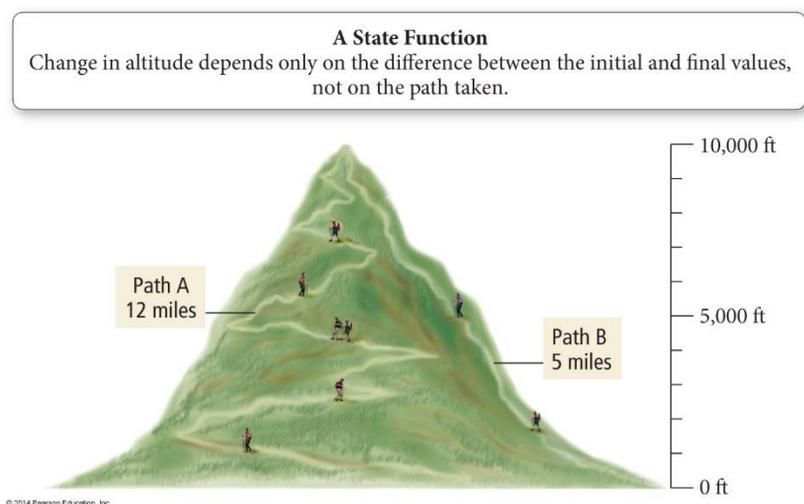
*All conversion factors in this table are exact.
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INTERNAL ENERGY

- Internal Energy (E) is the sum of the kinetic and potential energies of all of the particles that compose the system.



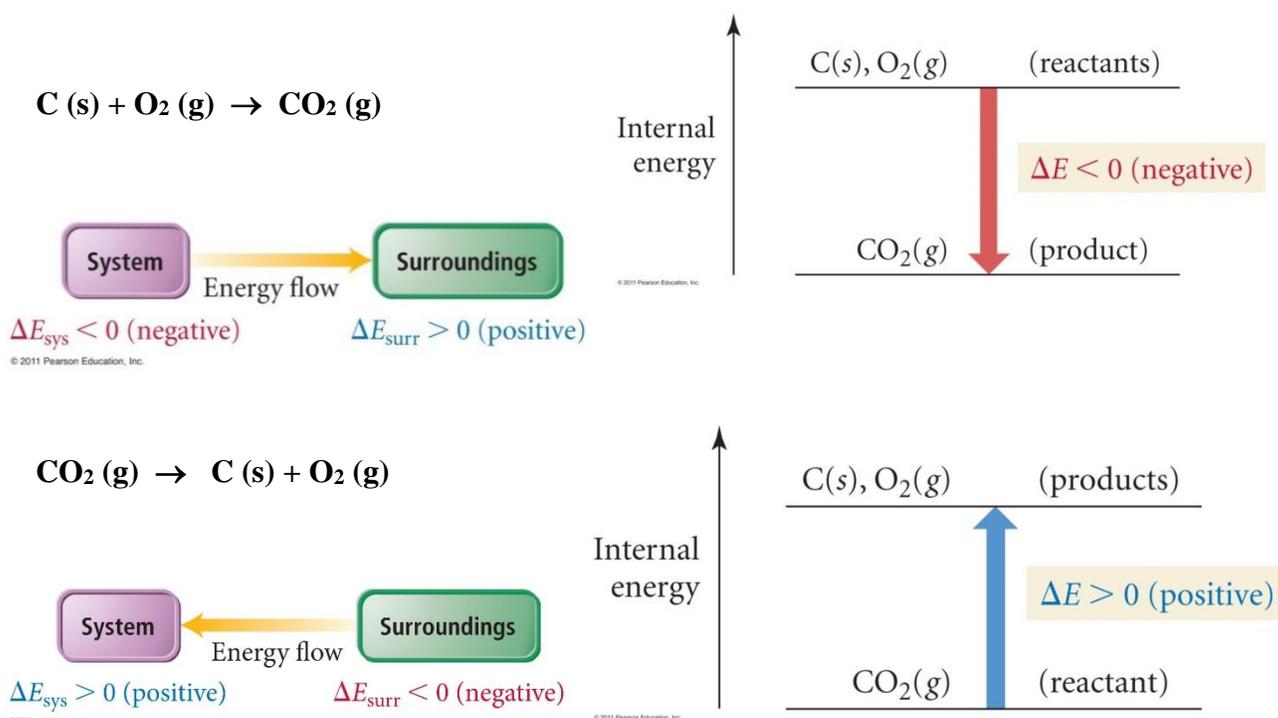
- Internal energy is a state function, which means its value only depends on the state of the system, and not how the system arrived at that state.



CHANGES IN INTERNAL ENERGY

- When a system changes from one state to another (ex: warming), its internal energy changes from one definite energy to another.
- Change in Internal Energy : $\Delta E = E_{\text{products}} - E_{\text{reactants}}$

where: E_{products} = final value of the internal energy
 $E_{\text{reactants}}$ = initial value of the internal energy

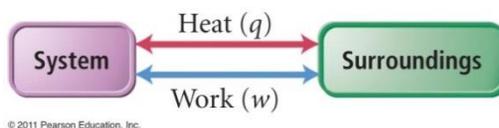


SUMMARY:

- If the reactants have higher internal energy than products, ΔE_{sys} is *negative* and energy flows out of the system and into the surroundings.
- If the reactants have lower internal energy than products, ΔE_{sys} is *positive* and energy flows into the system from the surroundings.

1ST LAW OF THERMODYNAMICS

- The changes in internal energy (ΔE) are more important in thermodynamics than the absolute values of Internal Energy
- The changes in IE are measured by noting the exchanges of energy between the system and the surroundings.
- These exchanges occur as one of two forms: **Heat** and **Work**



According to the *1st law of thermodynamics*, the changes in the internal energy of the system (ΔE) are the sum of the heat transferred (q) and the work done (w).

$$\Delta E = q + w$$

Heat (q) = the energy that moves into or out of the system because of a temperature difference between the system and its surroundings.

- When *heat is lost*, internal energy (E) *decreases* and q is therefore assigned a *negative sign*.
- When *heat is absorbed*, internal energy (E) *increases* and q is therefore assigned a *positive sign*.

Work (w) = the energy exchange that results when a force (F) moves an object through a distance (d).

$$\text{work} = \text{force} \times \text{distance}$$

- If *work is done by the system*, internal energy (E) *decreases* and w is therefore assigned a *negative sign*.
- If *work is done on the system*, internal energy (E) *increases* and w is therefore assigned a *positive sign*.

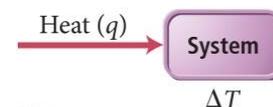
TABLE 6.3 Sign Conventions for q , w , and ΔE

q (heat)	+ system <i>gains</i> thermal energy	– system <i>loses</i> thermal energy
w (work)	+ work done <i>on</i> the system	– work done <i>by</i> the system
ΔE (change in internal energy)	+ energy flows <i>into</i> the system	– energy flows <i>out</i> of the system

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QUANTIFYING HEAT

- **Heat** is the exchange of energy between the system and surroundings, caused by a temperature difference. (Note the distinction between heat and temperature)
- Heat is the transfer of thermal energy, while **temperature** is a measure of thermal energy within a sample of matter. Thermal energy always flows from matter at higher temperature to matter at lower temperature.
- When a system absorbs heat, its temperature changes by ΔT . The heat absorbed by the system and its temperature change are directly proportional.



- The constant of proportionality between heat and temperature change is the system's **heat capacity**.

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

Heat capacity

- The heat capacity of a system is defined as the amount of heat required to change its temperature by 1°C . Heat capacity is an extensive property of matter (its value depends on the amount of matter).

$$C = \frac{q}{\Delta T} = \frac{\text{J}}{^\circ\text{C}}$$

- The measure of the intrinsic capacity of matter to absorb heat is its **specific heat capacity** (C_s).
- Specific heat capacity is defined as the amount of heat required to raise the temperature of 1 g of matter by 1°C . The units of specific heat capacity (also called specific heat) are $\text{J/g}^\circ\text{C}$.
- Listed to the right are specific heat capacity of several common substances. Note that water has the highest specific heat compared to the other substances—meaning that changing the temperature of water requires a lot of heat.
- Heat capacity is also sometimes reported as **molar heat capacity**, the amount of heat required to raise the temperature of 1 mole of a substance by 1°C . The units of molar heat capacity are $\text{J/mol}^\circ\text{C}$.

TABLE 6.4 Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity, C_s ($\text{J/g} \cdot ^\circ\text{C}$) [*]
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

^{*}At 298 K
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QUANTIFYING HEAT

- The specific heat of a substance can be used to quantify the amount of heat added to a substance and its corresponding temperature change. This relationship is shown below:

$$\text{Heat (J)} \rightarrow q = m \times C_s \times \Delta T$$

Temperature change (°C)

Mass (g)

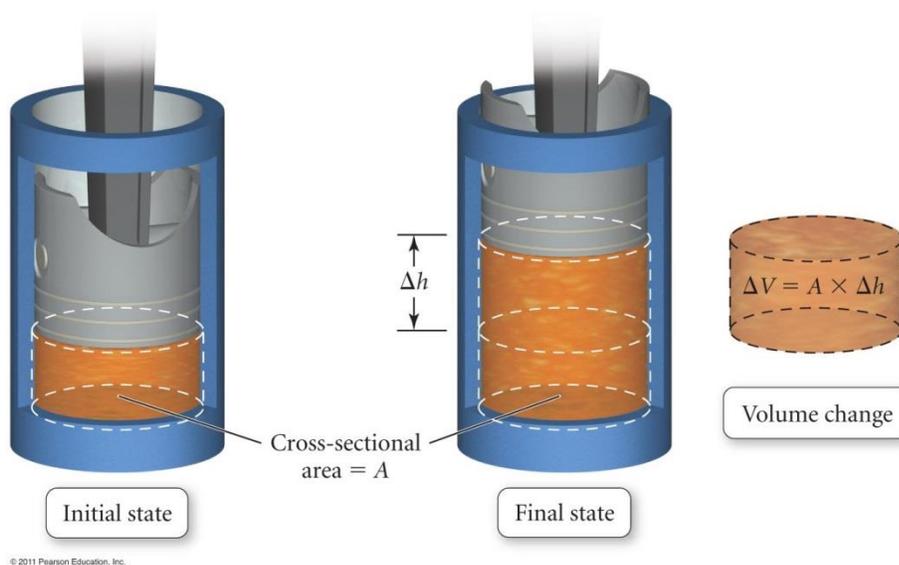
Specific heat capacity J/g · °C

Examples:

- How much heat is required to warm 1.50 kg of sand from 25.0°C to 100.0°C?
- A 55.0 g aluminum block initially at 27.5°C absorbs 725 J of heat. What is the final temperature of the aluminum?
- The amount of energy required to heat 2.0 g of carbon from 50.0°C to 80.0°C is 42.6 J. Based on this information, what is the molar heat capacity of carbon?

QUANTIFYING WORK (PRESSURE-VOLUME WORK)

- To calculate the work associated with a chemical reaction, we limit discussion to those associated with a volume change and therefore called *pressure-volume work*. Pressure-volume work occurs when the force is caused by a volume change against an external pressure.
- Assume a cylinder, where the pressure exerted by the atmosphere is replaced with a piston, whose downward force of gravity, F , creates a pressure on the gas equivalent to that of the atmosphere.



- When the volume of the cylinder increases, it pushes against the external force. The work done by the system in expanding = (Force of Gravity) x (Distance the piston moves)

$$w = F \times \Delta h$$

$$\text{since } \Delta V = A \times \Delta h$$

$$w = F \times \frac{\Delta V}{A} = \frac{F}{A} \times \Delta V$$

Atmospheric pressure (P)

- Since the volume of cylinder is increasing, work is done by the system and therefore assigned a negative sign.

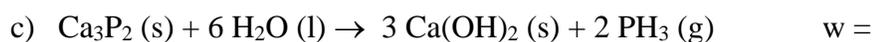
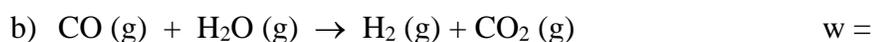
$$w = -P \Delta V$$

QUANTIFYING WORK

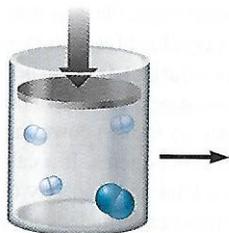
- In chemical systems, when gases *expand*, *work is done by the system*, and is therefore assigned a *negative* sign. When gases *contract*, *work is done on the system*, and therefore assigned a *positive* sign.
- Expansion occurs when there are more moles of gas produced in the reaction than originally present. Contraction occurs, when there are less moles of gas produced in the reaction than originally present.

Examples:

1. For each change shown below, determine if work is positive, negative or zero:



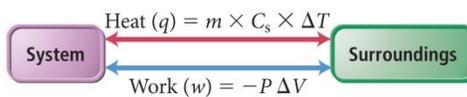
2. The diagram below shows a vessel with 1 molecule of $\text{N}_2 (\text{g})$ and 3 molecules of $\text{H}_2 (\text{g})$.



- a) Draw what the container will look like after a reaction has occurred to produce gaseous NH_3 . Assume constant pressure of 1 atm.
- b) Is the sign of work positive or negative or zero after the reaction?

CONSTANT-VOLUME (BOMB) CALORIMETRY

- Recall that the system and surroundings exchange energy in the form of heat or work. Also, recall that the change in internal energy that occurs during a chemical reaction (ΔE) is the sum of heat and work ($\Delta E = q + w$).



- Therefore, changes in temperature can be measured (to calculate heat) and changes in volume can be measured (to determine work), and then summed in order to calculate ΔE . Alternately, all the energy change associated with a chemical reaction can be forced to exhibit itself as heat, and then measured through the temperature change.
- Since work is product of pressure and change in volume, if the reaction is carried out at constant volume, then $\Delta V = 0$ and $w = 0$. The heat given off, called heat of constant volume (q_v) is equal to ΔE_{rxn} .

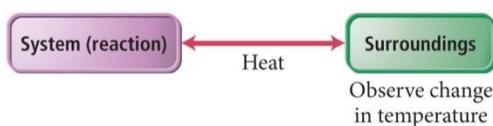
$$\Delta E_{\text{rxn}} = q_v + w$$

↙ Equals zero
at constant volume

$$\Delta E_{\text{rxn}} = q_v$$

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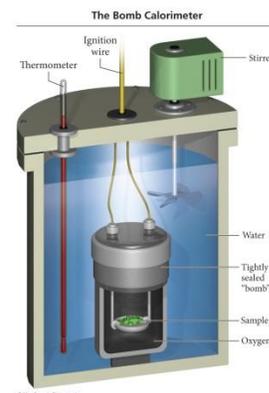
- Heat evolved in a reaction can be measured using a technique called **calorimetry**. In calorimetry, the heat exchanged between a reaction (system) and the surroundings is measured by the changes in temperature of the surroundings. The magnitude of the temperature change in the surroundings depends on the magnitude of ΔE and the heat capacity of the surroundings.



- Heat measurements described above can be done in a piece of equipment called a **bomb calorimeter**. A bomb calorimeter is designed to measure ΔE for combustion reactions. In these measurements, the reaction is carried out in a sealed container called a bomb, which ensures that the reaction occurs at constant volume.
- The temperature change (ΔT) is related to the heat absorbed by the entire calorimeter assembly (q_{cal}) as shown below:

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

where, C_{cal} is the heat capacity of the entire calorimeter assembly (determined separately).



ENTHALPY

- When a chemical reaction occurs at constant pressure—for example in an open beaker—the energy evolved can be in the form of both heat and work. The energy change (ΔE) for the reaction is the sum of the heat and work exchanged during the reaction.
- However, in many instances, only the heat evolved is of interest. At constant pressure, a thermodynamic quantity called *enthalpy* (H) represents this quantity.
- Enthalpy (H) of a system is defined as the sum of its internal energy and the product of pressure and volume:

$$H = E + PV$$

- Since internal energy, pressure and volume are all state functions, enthalpy is also a state function. The change in enthalpy (ΔH) for any process occurring at constant pressure can be determined as follows:

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

- The change in energy (ΔE) at constant pressure can be expressed as:

$$\Delta E = q_p + w$$

and

$$w = -P \Delta V$$

- Substituting these relationships into the equation for ΔH , we can arrive at the following:

$$\Delta H = (q_p + w) + P \Delta V$$

$$\Delta H = (q_p + w) + (-w)$$

$$\Delta H = q_p$$

- ΔH and ΔE are similar (both numerically and conceptually): they both represent change in a state function for the system. ΔE represents all the energy (heat and work) exchanged for the system, while ΔH represents only the heat exchanged for the system under conditions of constant pressure.
- For reactions that do not exchange much work with the surroundings—that is reactions that do not cause much volume change as they occur— ΔE and ΔH are nearly identical in value. For reactions that produce or consume large amounts of gas, and therefore result in large volume change, ΔE and ΔH can be slightly different in value.

ENTHALPY

- The signs of ΔH and ΔE follow the same convention. A chemical reaction with a **positive ΔH** indicates flow of heat into the system, as the reaction occurs. These reactions are called **endothermic**, and absorb heat from surroundings. As a result, these reactions are observed by a cooling of the surroundings.
- A chemical reaction with a **negative ΔH** indicates flow of heat out of the system, as the reaction occurs. These reactions are called **exothermic**, and release heat to the surroundings. As a result, these reactions are observed by a warming of the surroundings.

Examples:

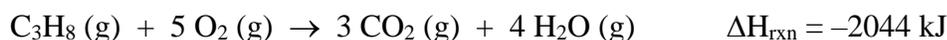
1. Lighters are usually fueled by butane (C_4H_{10}). When 1 mole of butane burns at constant pressure, it produces 2658 kJ of heat and does 3 kJ of work. What are the ΔH and ΔE for the combustion of butane in kJ/mol?

2. Identify each process as endothermic or exothermic and indicate the sign of ΔH :
 - e) sweat evaporating from skin
 - f) water freezing in a freezer
 - g) wood burning in a fire

- 3.

THERMOCHEMICAL EQUATIONS

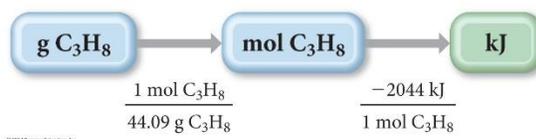
- The enthalpy change for a reaction (ΔH_{rxn}) is also called *enthalpy of reaction* or *heat of reaction*. The heat of reaction is an extensive property of matter, one that depends on the amount of matter undergoing the reaction.
- The ΔH_{rxn} reported with an equation, is the heat absorbed or released based on the stoichiometric amounts of reactants or products. Such an equation is called *thermochemical equation*. For example:



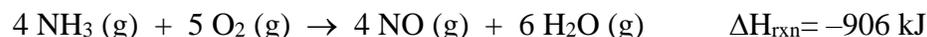
- Based on the equation above, the following equalities can be determined:

$$1 \text{ mol C}_3\text{H}_8 = -2044 \text{ kJ} \quad \text{or} \quad 5 \text{ mol O}_2 = -2044 \text{ kJ}$$

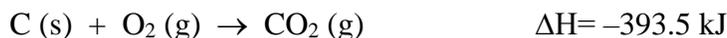
- These equalities can be used to construct conversion factors to solve stoichiometric problems involving heat absorbed or produced in a reaction. For example, the following conceptual plan can be used to determine kJ of heat produced based on grams of C_3H_8 burned:


Examples:

- Calculate the heat associated with the complete reaction of 155 g of NH_3 , as shown below:

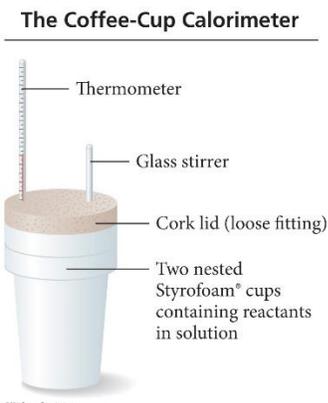


- Charcoal is primarily carbon. Determine the mass of CO_2 produced by burning enough carbon (in the form of charcoal) to produce 5.00×10^2 kJ of heat.



CONSTANT-PRESSURE CALORIMETRY

- For many aqueous reactions, the ΔH_{rxn} can be measured using a coffee-cup calorimeter. This type of calorimeter is insulated from the surroundings by inserting two coffee cups into each other and is also equipped with a thermometer and a stirrer.
- The reaction occurs in a specifically measured amount of solution in the calorimeter, so that the mass of solution is known. During the reaction, the heat evolved or absorbed causes a temperature change in the solution, which is measured with the thermometer.
- The heat absorbed or lost by the solution can be calculated knowing the specific heat of the solution (normally assumed to be that of water) as shown below:



$$q_{\text{soln}} = (m \times C_s \times \Delta T)_{\text{soln}}$$

- Since the calorimeter is insulated from the surroundings, we assume the heat gained by the solution is the heat lost by the reaction (or vice versa):

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

- Since the reaction occurs under the conditions of constant pressure (open to the atmosphere):

$$q_{\text{rxn}} = q_p = \Delta H_{\text{rxn}}$$

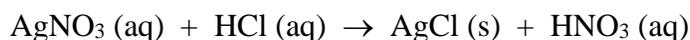
- The heat measured this way is based on a specific amount of reactant (measured ahead of time) and can be converted into kJ per mole.

Summarizing Calorimetry:

- *Bomb calorimetry* occurs at *constant volume* and measures ΔE for a reaction.
- *Coffee-cup calorimetry* occurs at *constant pressure* and measures ΔH for a reaction.

CONSTANT-PRESSURE CALORIMETRY**Examples:**

1. When 50.0 mL of 0.100 M AgNO₃ is combined with 50.0 mL of 0.100 M HCl in a coffee-cup calorimeter, the temperature changes from 23.40°C to 24.21°C. Calculate ΔH_{rxn} (in kJ/mol) for the reaction shown below. (Assume density and specific heat of solutions to be the same as water)



2. The same reaction, with exactly the same amount of reactant, is conducted in a bomb calorimeter and in a coffee-cup calorimeter. In one measurement, $q_{\text{rxn}} = -12.5$ kJ and in the other $q_{\text{rxn}} = -11.8$ kJ. Which value was obtained in the bomb calorimeter? (Assume the reaction has a positive ΔV in the coffee-cup calorimeter)
3. When 13.4 g of NH₄Cl is dissolved in 0.500 L of pure water in a coffee-cup calorimeter, the temperature of water decreased from 21.4°C to 17.8°C. Calculate the ΔH_{rxn} for NH₄Cl in kJ/mol. (Assume specific heat of the solution to be the same as water)

RELATIONSHIPS INVOLVING ΔH_{rxn}

- The change in enthalpy of a reaction is always associated with a particular reaction. If the reaction is changed, then the ΔH also changes accordingly. Three such changes are listed below:

- If the equation is multiplied by a factor, then the ΔH is also multiplied with the same factor.**



- If a chemical equation is reversed, then the ΔH changes sign.**



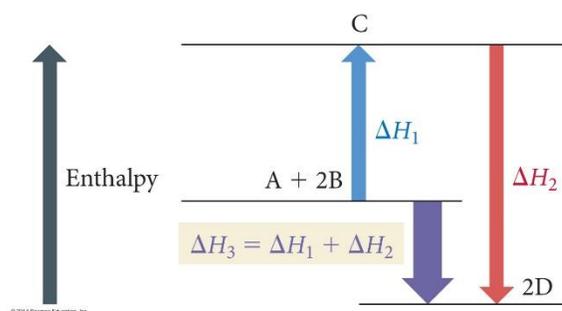
- If a chemical reaction can be expressed as the sum of a series of steps, then the ΔH_{rxn} for the overall equation is the sum of the heat of reaction of each step.**



- This relationship is called *Hess's law*.

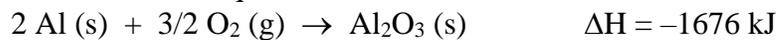
Hess's Law

The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.

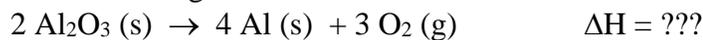


RELATIONSHIPS INVOLVING ΔH_{rxn}
Examples:

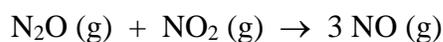
1. Given the thermochemical equation below:



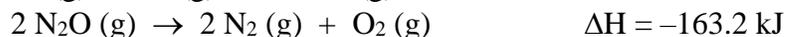
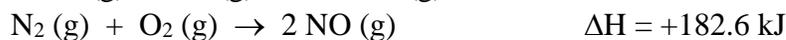
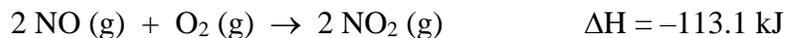
find ΔH for the following reaction:



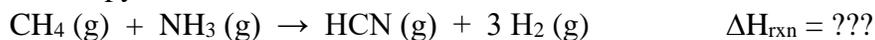
2. Find ΔH_{rxn} for the reaction:



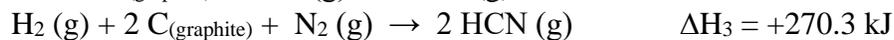
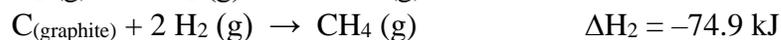
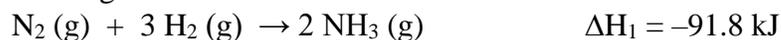
from the following reactions with known ΔH 's:



3. Calculate the enthalpy of reaction for the reaction shown below:

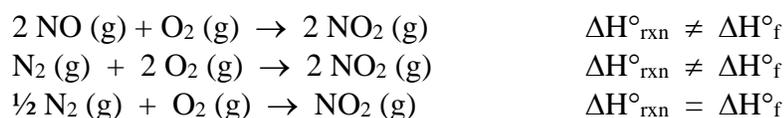


From the following:

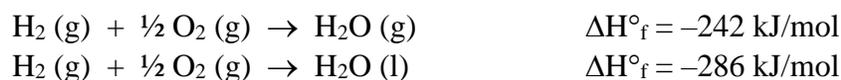


ENTHALPIES OF FORMATION

- In order to study enthalpy changes more clearly, we define a standard state, where enthalpy changes can be measured relative to. The standard state is defined as:
 - **Gases:** pure gas at a pressure of exactly 1 atm.
 - **Liquid or Solid:** pure substance in its most stable form at a pressure of 1 atm and temperature of 25°C.
 - **Solution:** concentration of exactly 1 M.
- The change in enthalpy for a process where all reactants and products are in their standard states is called the **standard enthalpy change** (ΔH°).
- The change in enthalpy when one mole of a substance is formed from its constituent elements in their standard states is called the **standard enthalpy (or heat) of formation** (ΔH_f°). These values are available in textbooks or other reference material.
- For example, consider the 3 equations shown below. All 3 describe the formation of NO₂, but only one of these properly describes the enthalpy of formation for NO₂.



- Also, note that when determining the enthalpy of formation, the state of each substance is important and determines the values determined, as shown below:



- The standard heat of formation for an element in its standard state is zero.
- The standard heat of formation for a compound is always written to form one mole. Therefore, the units of ΔH_f° are kJ/mol.
- The standard enthalpy of reaction ($\Delta H^\circ_{\text{rxn}}$) can be calculated from the standard enthalpies of formation (ΔH_f°) as shown below:

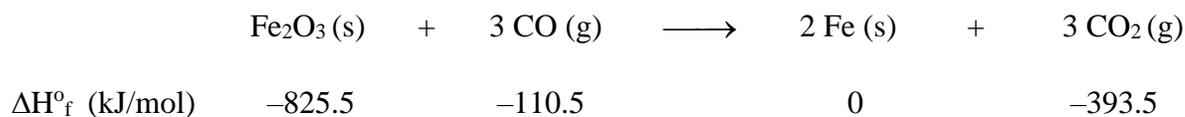
$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

where,

n and m are the stoichiometric coefficients of the products and reactants in the reaction

ENTHALPIES OF FORMATION
Examples:

1. Iron is obtained from iron ore by reduction with carbon monoxide. The overall reaction is shown below. Calculate the standard enthalpy change for this reaction.



2. Calculate the standard enthalpy of formation for ethylene (C_2H_2) from the standard enthalpies of reaction shown below:

