

CHEMICAL REACTIONS INVOLVE ENERGY

The study of energy and its transformations is known as thermodynamics.

The discussion of thermodynamics involve the concepts of energy, work, and heat.

Types of Energy

Potential energy is stored energy that matter possesses as result of its composition or position relative to other objects.

$$E_p = mgh$$

Kinetic energy is energy matter has as a result of its motion.

$$K_E = \frac{1}{2}mv^2$$

Chemical energy is due to potential energy stored in arrangements of atoms of the substance.

Likewise, the energy an object possesses because of its temperature (thermal energy) is associated with the kinetic energy of the molecules in the object.

COMMON MISCONCEPTIONS

Don't confuse power and energy or heat and temperature.

Heat is the energy that is transferred from a hotter object to a colder one.

Energy is the capacity to do work or to transfer heat.

Power is the time rate at which work is done or energy transferred.

Temperature is a measure of average kinetic energy of a substance.

ENERGY UNITS

The SI unit for energy is the joule.

With mass expressed in kilograms and velocity expressed in meter per seconds, kinetic energy has the units of joules ($1\text{J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2$).

A joule is not a large amount of energy, thus kilojoules (kJ) is often used.

Traditionally, energy changes accompanying chemical reactions have been expressed in calories.

A calorie (cal) was originally defined as the amount of energy required to raise the temperature of 1 g of water by 1 °C. It is now defined in terms of the joule:

$$1\text{ cal} = 4.184\text{ J (exactly)}$$

A related energy unit used in nutrition is the nutritional Calorie. $1\text{ Cal} = 1\text{ kcal}$

SYSTEMS AND SURROUNDINGS

When we study energy changes, we focus our attention on a limited and well-defined part of the universe. The portion we single out for study is called the **system**; everything else is called the **surroundings**.

If we observe a chemical reaction in the lab, the chemicals usually constitute the system. The container and everything beyond it are considered the surroundings.

The systems we can most readily study are called closed systems (matter can't be exchanged with the surrounding).

THE FIRST LAW OF THERMODYNAMICS

Science has observed that energy can be neither created nor destroyed: *energy is conserved*.

Any energy lost by the system must be gained by the surroundings, and vice versa.

This important fundamental observation is known as the first law of thermodynamics, which is also called the *law of conservation of energy*.



INTERNAL ENERGY

The total energy of a system is the sum of all the kinetic and potential energies of its component parts.

Parts being O₂ and H₂ molecules.

We define the change in internal energy as the difference between the internal energy of the system at the completion of a process and that at the beginning:

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

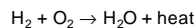
The quantity ΔE has three parts: a number, a unit, and a sign.

A positive ΔE results when $E_{\text{final}} > E_{\text{initial}}$, thus the system has gained energy from its surrounding.

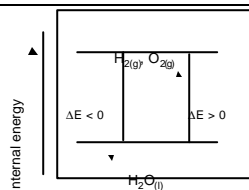
A negative ΔE results when $E_{\text{final}} < E_{\text{initial}}$, here the system has lost energy to its surroundings.

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

In a chemical reaction the initial state of the system refers to the reactants and the final state refers to the products.



When hydrogen and oxygen form water, the system loses energy to the surroundings as heat; the energy content of the products is less than that of the reactants, thus ΔE is negative.



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RELATING ΔE TO HEAT AND WORK

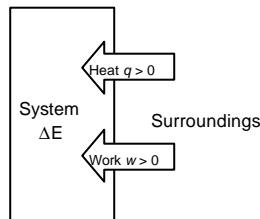
Any system can exchange energy with its surroundings in two general ways: as heat or work.

When a system undergoes any chemical or physical change, the accompanying change in its internal energy, ΔE , is given by the heat added to or liberated from the system, q , plus the work done on or by the system, w .

$$\Delta E = q + w$$

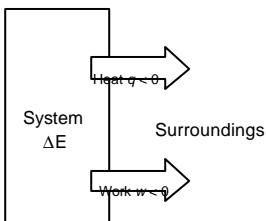
This is the first law of thermodynamics in algebraic form.

When Heat is transferred from the surrounding to the system, q has a positive value.



Likewise, when work is done on the system by the surrounding, w has a positive value.

When Heat is transferred from the system to the surroundings, q has a negative value.



Likewise, when work is done on the surroundings by the system, w has a negative value.



The H_2 and O_2 gases in the cylinder are ignited. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves up and does 480 J of work on the surroundings. What is the change in internal energy of the system?

ENDOTHERMIC AND EXOTHERMIC PROCESSES

When a process occurs in which the system absorbs heat, we say the process endothermic (endo = into).

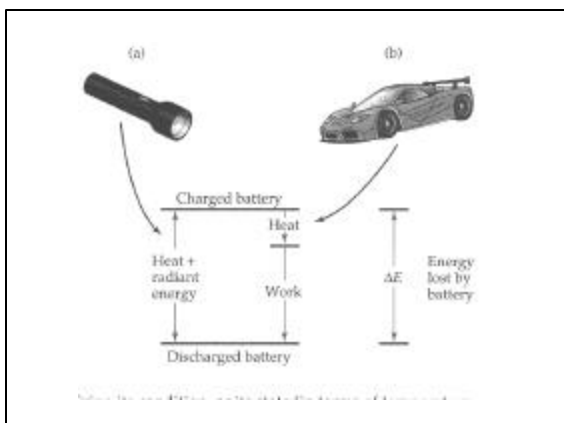
A process that results in the evolution of heat is called exothermic (exo = out of).



STATE FUNCTIONS

One has no way of knowing the precise value of the internal energy of a system, however one does know that it has a fixed value for a given set of conditions. The conditions that influence this energy include the temperature and pressure. And energy is an extensive property.

State functions do not depend on the pathway, only on the initial and final states.



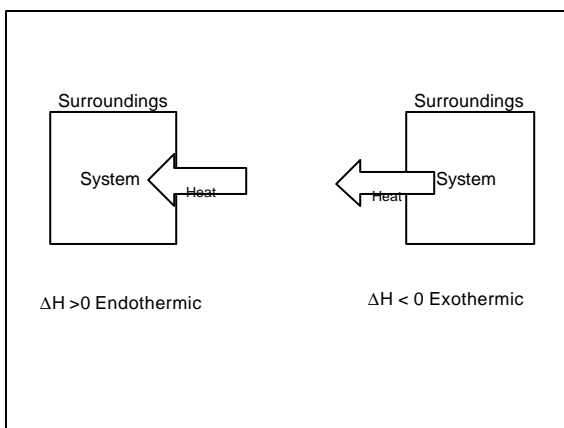
$$\Delta E = q + w$$

ENTHALPHY

A quantity defined by the relationship $H = E + PV$.

The enthalpy change, ΔH for a reaction that occurs at constant pressure, is the heat evolved or absorbed in the reaction: $\Delta H = q_p$

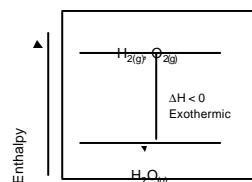
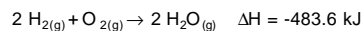
In short, enthalpy is a convention used to make the measuring of heats of reaction simple by removing work.



ENTHALPIES OF REACTION

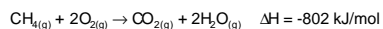
The enthalpy change for a chemical reaction is given by the enthalpy of the products minus that of the reactants:

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

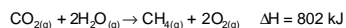


GUIDELINES FOR USING THERMOCHEMICAL EQUATIONS

1. Enthalpy is an extensive property.



2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.



3. The enthalpy change for a reaction depends on the state of the reactants and products.



The value of ΔH can be determined experimentally by measuring the heat flow accompanying a reaction. When heat flows into or out of a substance, the temperature of the substance changes.

Experimentally, we can determine the heat flow associated with a chemical reaction by measuring the temperature change it produces. The measurement of heat flow is calorimetry; an apparatus that measures heat flow is a calorimeter.

HEAT CAPACITY AND SPECIFIC HEAT

The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its heat capacity.

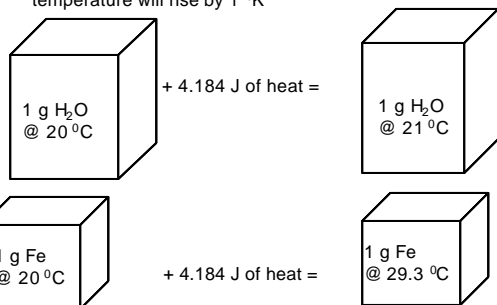
For pure substances the heat capacity is usually given for a specified amount of the substance. The heat capacity of 1 mole of substance is called its molar heat capacity.

The heat capacity of 1 g of a substance is called specific heat capacity, or just its specific heat.

$$\text{Specific heat} = \frac{\text{Quantity of heat transferred}}{(\text{grams of substance}) \times (\text{temperature change})}$$

$$\text{Specific heat} = \frac{q}{m \times \Delta T}$$

If one +4.184 J of heat is added to 1 gram of water its temperature will rise by 1 °K



How much heat is required to heat 300.0g of water from 22 °C to 100 °C?

$$\text{Specific heat} = \frac{q}{m \times \Delta T} \quad \leftarrow \text{Solve for } q$$

$$q = (\text{spec. heat of water})(m \times \Delta T)$$

$$(4.184 \text{ J/g} \times \text{K})(300\text{g})(78 \text{ K}) = 97.91 \text{ kJ}$$

CONSTANT-PRESSURE CALORIMETRY

Many solution reactions occur at constant pressure so that $\Delta H = q_p$

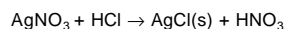
$$q_{\text{rxn}} = -q_{\text{soln}}$$

$$q_{\text{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T$$



When 50.0 mL of 0.100M AgNO₃ and 50.0mL of 0.100M HCl are mixed in a calorimeter, the temperature of the mixture increase from 22.3 to 23.11 °C

Calculate ΔH for this reaction:



Assume that the combined solution has a mass of 100g and specific heat of 4.184J/g°C

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

$$q_{\text{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T$$

$$(4.184\text{J/g}^\circ\text{C})(100\text{g})(0.81) = 338.9 \text{ J}/0.005 \text{ moles}$$

$$\Delta H = -67.8 \text{ kJ}$$

CONSTANT VOLUME CALORIMETRY

Calculate the heat capacity of a calorimeter ($C_{\text{calorimeter}}$).

Combustion of exactly 1g of benzoic acid produces 26.38 kJ of heat.

When 1g of benzoic acid is combusted in our calorimeter it causes a temperature increase of 5.022 °C.

The heat capacity of the calorimeter is:

$$\frac{26.38 \text{ kJ}}{5.022 \text{ }^\circ\text{C}} = 5.022 \text{ kJ/}^\circ\text{C}$$

CONSTANT VOLUME CALORIMETRY

If 1g hydrazine, which has a heat of reaction of -618kJ/mol, is combusted in a calorimeter, that has a heat capacity of 5.022kJ/°C, what will be the expected rise in temperature?

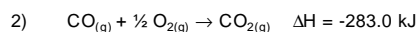
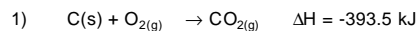
$$\left(\frac{618 \text{ kJ}}{\text{mol}} \right) \left(\frac{^\circ\text{C}}{5.022 \text{ kJ}} \right) (1 \text{ g N}_2\text{H}_4) \left(\frac{1 \text{ mol N}_2\text{H}_4}{32.0 \text{ g}} \right) = 3.85 \text{ }^\circ\text{C}$$

HESS'S LAW

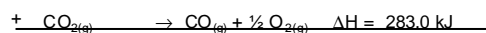
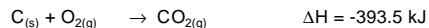
If a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps.

ΔH for any process can be calculated using ΔH values from other reactions.

Using the following enthalpies of combustion:



calculate the enthalpy of combustion for the combustion of C to CO.



ENTHALPIES OF FORMATION

The heat of reaction for many chemical reactions can be calculated from a few tabulated ΔH values.

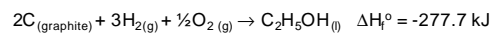
Extensive tables exist of *enthalpies of vaporization* for converting liquids to gas, *enthalpies of fusion* for converting liquid to solids) and *enthalpies of combustion*.

An important process used for tabulating thermochemical data is the formation of a compound from its constituent elements. This is called the *enthalpy of formation* ΔH_f .

In order to compare the enthalpies of different reactions, it is convenient to define a set of conditions, called a standard state, at which most enthalpies are tabulated. The *standard state* of a substance is its pure form at atmospheric pressure and 298K (25 °C).

The standard enthalpy of a reaction is defined as the enthalpy changed when all reactants and products are in their standard state. We denote a standard enthalpy as ΔH° , where the superscript $^\circ$ indicates standard-state conditions

The **standard enthalpy of formation** of a compound, ΔH_f° is the change in enthalpy for the reaction that forms 1 mole of the compound from its elements, with all substances in their standard states.



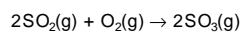
If an element exists in more than one form under standard conditions, the most stable form of that element is used for the formation reaction.

Using Enthalpies of formation to Calculate ΔH_{rxn}

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

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

Use standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^\circ$ for the reaction:



$$\Delta H_f^\circ, \text{ kJ/mol} \quad -296.83 \quad 0 \quad -395.72$$

From Appendix C p987

$$\Delta H_{\text{rxn}}^\circ = [2 \text{ mol SO}_3 \cdot \Delta H_f^\circ(\text{SO}_3)] - [2 \text{ mol SO}_2 \cdot \Delta H_f^\circ(\text{SO}_2) + 1 \text{ mol O}_2 \cdot \Delta H_f^\circ(\text{O}_2)]$$

$$[2(-395.72)] - [2(-296.83) + 1(0)] = -197.78 \text{ kJ}$$