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Potassium reacts with water, liberating sufficient heat to ignite the hydrogen evolved. The transfer of heat between substances in chemical reactions is an important aspect of thermochemistry.

Thermochemistry

References : 1. General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette)
2. Chemistry-10th Edition (Raymond Chang)

The chemistry that deals with energy exchange, entropy, and the spontaneity of a chemical process.

Thermochemistry *is the branch of chemistry concerned with the heat* effects that accompany chemical reactions. To understand the relationship between heat and chemical and physical changes, we must start with some basic definitions.

Getting Started: Some Terminology

- Energy” is a much-used term that represents a rather abstract concept. It cannot be seen, touched, smelled, or weighed. ***Energy is usually defined as the capacity to do work.***
- **Work** is done when a force acts through a distance. Moving objects do work when they slow down or are stopped.
- ***Kinetic energy is defined as*** *the energy produced* by a moving object.
- ***Thermal energy is the energy associated with the random motion of atoms and*** *molecules.*
- **Potential energy is** an energy associated with forces of attraction or repulsion between objects.
- ***Chemical energy is stored within the structural units of chemical substances***

- All forms of energy can be converted (at least in principle) from one form to another. We feel warm when we stand in sunlight because radiant energy is converted to thermal energy on our skin. When we exercise, chemical energy stored in our bodies is used to produce kinetic energy. When a ball starts to roll downhill, its potential energy is converted to kinetic energy.
- Although energy can assume many different forms that are interconvertible, scientists have concluded that energy can be neither destroyed nor created. When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is summarized by the ***law of conservation of energy: the total quantity of energy in the universe is assumed*** *constant.*

Almost all chemical reactions absorb or produce (release) energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. ***Heat*** ***is the transfer of thermal energy between two bodies that are at different*** *temperatures. Thus, we often speak of the "heat flow" from a hot object to a cold* one. Although the term "heat" by itself implies the transfer of energy, we customarily talk of "heat absorbed" or "heat released" when describing the energy changes that occur during a process.

Thermochemistry is the study of heat change in chemical *reactions.*

To analyze energy changes associated with chemical reactions we must first define the ***system, or the specific part of the universe that is of interest to us.***

There are three types of systems. An ***open system can exchange mass and energy,*** *usually in the form of heat with its surroundings. For example, an open system may* consist of a quantity of water in an open container, as shown in Figure 6.1 (a). If we close the flask, as in Figure 6.1 (b), so that no water vapor can escape from or condense into the container, we create a ***closed system, which allows the transfer of energy*** *(heat) but not mass. By placing the water in a totally insulated container, we can* construct an ***isolated system, which does not allow the transfer of either mass or*** *energy, as shown in Figure 6.1 (c).*

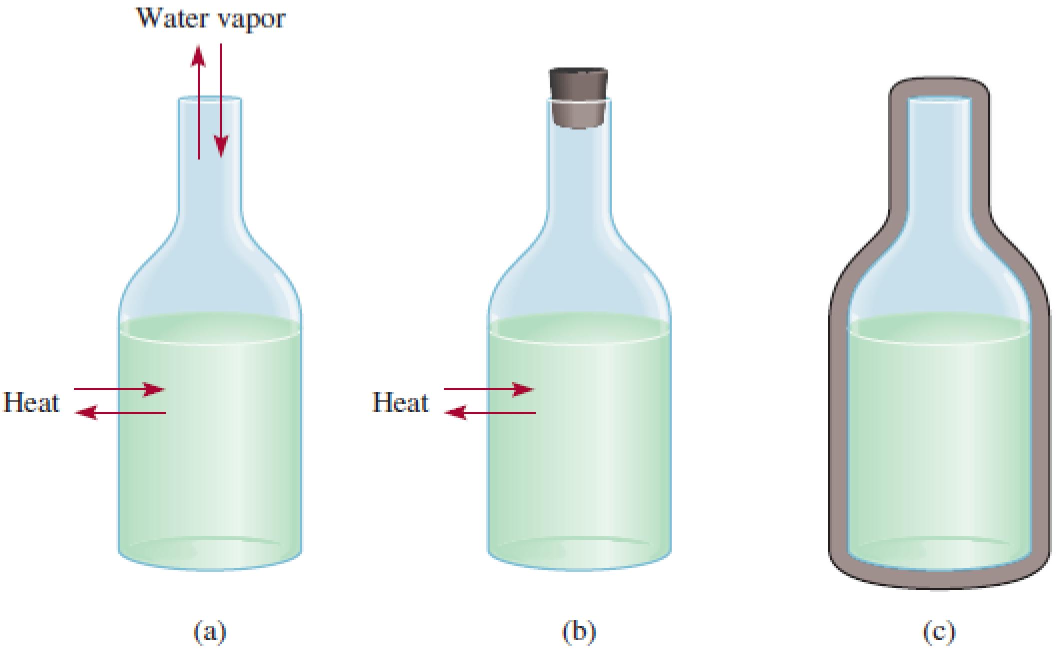

Figure 6.1 *Three systems represented by water in a flask: (a) an open system, which allows the exchange of both energy and mass with surroundings; (b) a closed system, which allows the exchange of energy but not mass; and (c) an isolated system, which allows neither energy nor mass to be exchanged (here the flask is enclosed by a vacuum jacket).*

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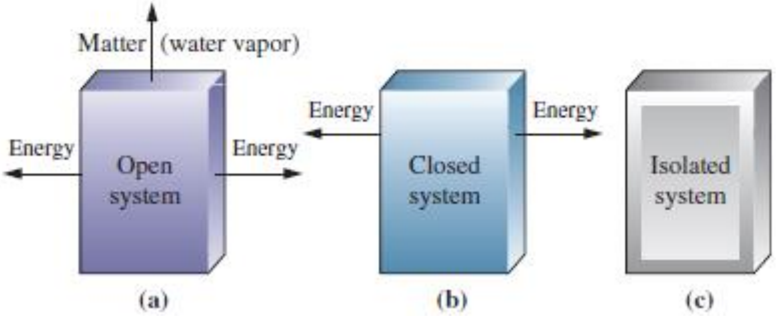
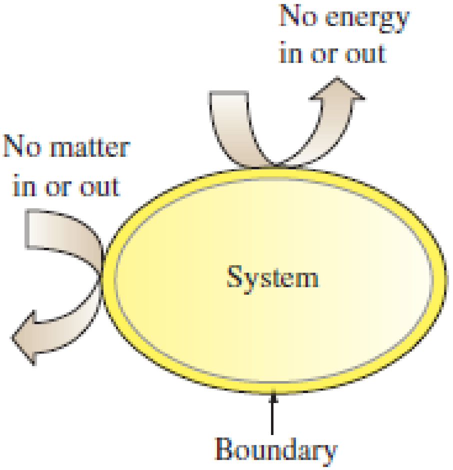
Systems and their surroundings
(a) *Open system*. The beaker of hot coffee transfers energy to the surroundings—it loses heat as it cools. Matter is also transferred in the form of water vapor. **(b)** *Closed system*. The flask of hot coffee transfers energy (heat) to the surroundings as it cools. Because the flask is stoppered, no water vapor escapes and no matter is transferred.
(c) *Isolated system*. Hot coffee in an insulated container approximates an isolated system. No water vapor escapes, and, for a time at least, little heat is transferred to the surroundings. (Eventually, though, the coffee in the container cools to room temperature.)





▲ Isolated system
Neither energy nor matter is transferred between the system and its surroundings.

The **surroundings are that part of the universe outside the system with which the** system interacts.

The First Law of Thermodynamics

The ***first law of thermodynamics, which is based on the law of conservation of energy,*** states that *energy can be converted from one form to another, but cannot be created or destroyed.*

We can test the validity of the first law by measuring only the *change in the internal energy of a system between its initial state and* its *final state in a process. The change in internal energy* ΔE *is given by*

$$\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}}$$

where E_i *and* E_f *are the internal energies of the system in the initial and final states,* respectively.

The internal energy of a system has two components: kinetic energy and potential energy. The kinetic energy component consists of various types of molecular motion and the movement of electrons within molecules. Potential energy is determined by the attractive interactions between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interaction between molecules.

It is impossible to measure all these contributions accurately, so we cannot calculate the total energy of a system with any certainty. Changes in energy, on the other hand, can be determined experimentally.

Work

We have seen that work can be defined as force *F* multiplied by distance *d*:

$$w = F \times d \tag{6.2}$$

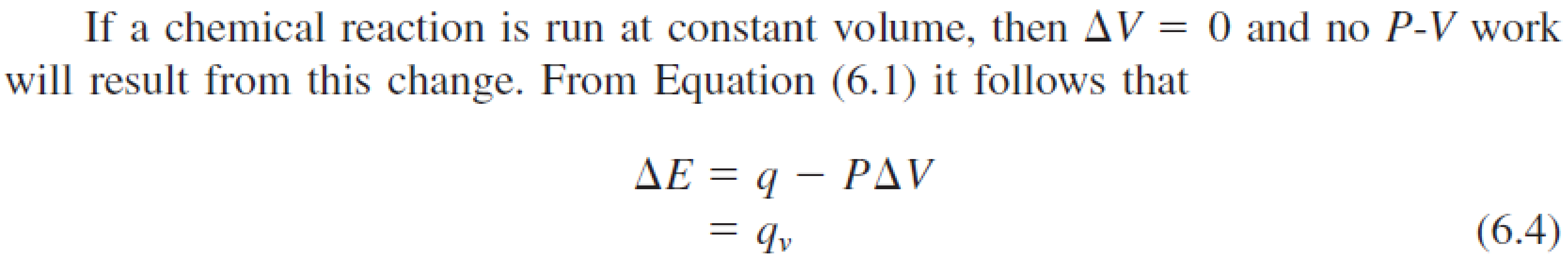
Heat is energy transferred between a system and its surroundings as a result of a temperature difference. Energy that passes from a warmer body (with a higher temperature) to a colder body (with a lower temperature) is transferred as heat.

At the molecular level, molecules of the warmer body, through collisions, lose kinetic energy to those of the colder body.

Thermal energy is transferred—“heat flows”—until the average molecular kinetic energies of the two bodies become the same, until the temperatures become equal. Heat, like work, describes energy in transit between a system and its surroundings.

Enthalpy of Chemical Reactions

Our next step is to see how the first law of thermodynamics can be applied to processes carried out under different conditions. Specifically, we will consider two situations most commonly encountered in the laboratory; one in which the volume of the system is kept constant and one in which the pressure applied on the system is kept constant.



If a chemical reaction is run at constant volume, then $\Delta V = 0$ and no P-V work will result from this change. From Equation (6.1) it follows that

$$\begin{aligned}\Delta E &= q - P\Delta V \\ &= q_v \qquad (6.4)\end{aligned}$$

Enthalpy

Constant-volume conditions are often inconvenient and sometimes impossible to achieve. Most reactions occur under conditions of constant pressure (usually atmospheric pressure). If such a reaction results in a net increase in the number of moles of a gas, then the system does work on the surroundings (expansion). This follows from the fact that for the gas formed to enter the atmosphere, it must push the surrounding air back. Conversely, if more gas molecules are consumed than are produced, work is done on the system by the surroundings (compression). Finally, no work is done if there is no net change in the number of moles of gases from reactants to products.

In general, for a constant-pressure process we write

$$\begin{aligned} \Delta E &= q + w \\ &= q_p - P\Delta V \end{aligned}$$

or

$$q_p = \Delta E + P\Delta V \tag{6.5}$$

where the subscript "p" denotes constant-pressure condition.

Indirect Determination of ΔH: Hess's Law

One of the reasons that the enthalpy concept is so useful is that a large number of heats of reaction can be calculated from a small number of measurements. The following features of enthalpy change make this possible.

- **$\Delta_r H°$ Depends on the Way the Reaction is Written.** Consider the standard enthalpy change in the formation of NO(g) from its elements at 25 °C.

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta_r H° = 180.50\ \text{kJ mol}^{-1}$$

To express the enthalpy change in terms of *one mole* of NO(g), we divide all coefficients *and the $\Delta_r H$ value* by *two*.

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta_r H° = \frac{1}{2} \times 180.50 = 90.25\ \text{kJ mol}^{-1}$$

- **$\Delta_r H°$ Changes Sign When a Process Is Reversed.** As we learned on page 261, if a process is reversed, the change in a function of state reverses sign. Thus, $\Delta_r H°$ for the *decomposition* of one mole of NO(g) is $-\Delta_r H°$ for the *formation* of one mole of NO(g).

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \quad \Delta_r H° = -90.25\ \text{kJ mol}^{-1}$$

- **Hess's Law of Constant Heat Summation.** To describe the standard enthalpy change for the formation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$,

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta_r H° = ?$$

Key Equations

$\Delta E = q + w$	Mathematical statement of the first law of thermodynamics.
$w = -P\Delta V$	Calculating work done in gas expansion or gas compression.
$H = E + PV$	Definition of enthalpy.
$\Delta H = \Delta E + P\Delta V$	Calculating enthalpy (or energy) change for a constant-pressure process.
$C = ms$	Definition of heat capacity.
$q = ms\Delta t$	Calculating heat change in terms of specific heat.
$q = C\Delta t$	Calculating heat change in terms of heat capacity.
$\Delta H^\circ_{\text{rxn}} = \Sigma n\Delta H^\circ_{\text{f}}\,(\text{products}) - \Sigma m\Delta H^\circ_{\text{f}}\,(\text{reactants})$	Calculating standard enthalpy of reaction.

Spontaneous Processes

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions (for example, at a certain temperature, pressure, and concentration). This knowledge is important whether one is synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale, or trying to understand the intricate biological processes in a cell. A reaction that *does occur under the given set of conditions is called a spontaneous reaction. If a reaction does not occur under specified conditions, it is said to be nonspontaneous.*

Entropy

In order to predict the spontaneity of a process, we need to introduce a new thermodynamic quantity called entropy. ***Entropy (S) is often described as a measure of how*** *spread out or dispersed the energy of a system is among the different possible ways that system can contain energy.*

A thermodynamic (*energy*) function that describes the degree of ***randomness*** or ***probability*** of existence.

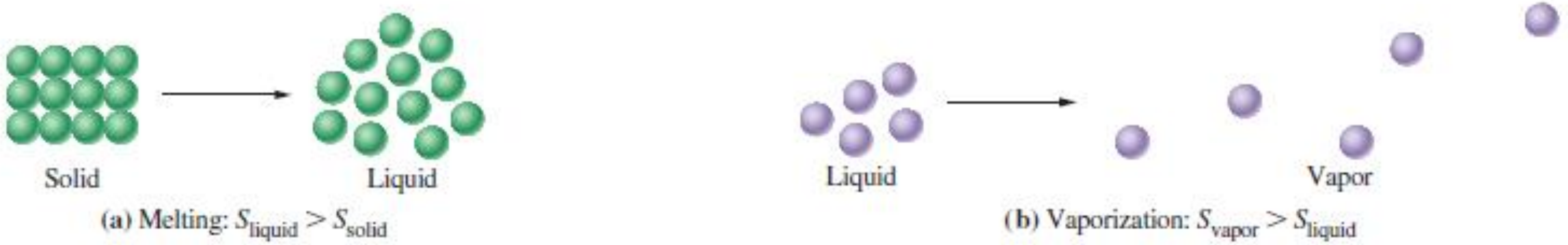
As a *state function* – entropy change depends only on the initial and final states, but not on how the change occurs.

The driving force for a spontaneous process is an increase in the entropy of the universe.

What is the significance of *entropy*?

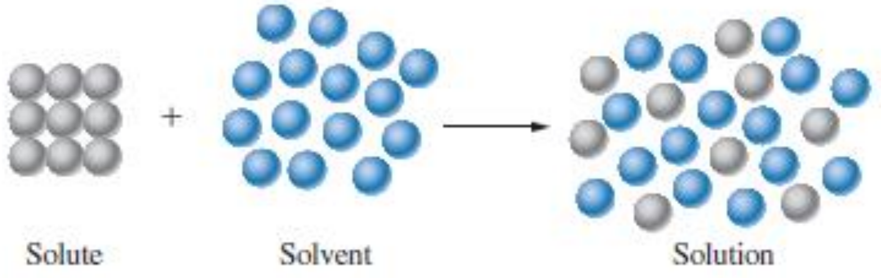
Nature spontaneously proceeds toward the state that has the highest probability of (energy) existence – highest entropy

Entropy is used to predict whether a given process/reaction is thermodynamically possible;



(a) Melting: $S_{\text{liquid}} > S_{\text{solid}}$

(b) Vaporization: $S_{\text{vapor}} > S_{\text{liquid}}$



(c) Dissolving: $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$

▲ FIGURE 13-4

Three processes in which entropy increases

Each of the processes pictured—**(a)** the melting of a solid, **(b)** the evaporation of a liquid, and **(c)** the dissolving of a solute—results in an increase in entropy. For part (c), the generalization works best for nonelectrolyte solutions, in which ion–dipole forces do not exist.

In summary, four situations generally produce an *increase* in entropy:

- Pure liquids or liquid solutions are formed from solids.
- Gases are formed from either solids or liquids.
- The number of molecules of gas increases as a result of a chemical reaction.
- The temperature of a substance increases. (Increased temperature means an increased number of accessible energy levels for the increased molecular motion, whether it be vibrational motion of atoms or ions in a solid, or translational and rotational motion of molecules in a liquid or gas.)

The Second Law of Thermodynamics

The connection between entropy and the spontaneity of a reaction is expressed by the ***second law of thermodynamics: The entropy of the universe increases in a spontaneous*** *process and remains unchanged in an equilibrium process.*

Because the universe is made up of the system and the surroundings, the entropy change in the universe (Δ*Suniv) for any process is the sum of the entropy changes in the system* (Δ*Ssys) and in the surroundings (*Δ*Ssurr).*

Mathematically, we can express the second law of thermodynamics as follows:

For a spontaneous process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{18.4}$$

For an equilibrium process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \tag{18.5}$$

Entropy Changes in the System

To calculate ΔS_{univ}, we need to know both ΔS_{sys} and ΔS_{surr}. Let us focus first on ΔS_{sys}. Suppose that the system is represented by the following reaction:

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

As is the case for the enthalpy of a reaction [see Equation (6.18)], the ***standard entropy of reaction*** ΔS°_{rxn} is given by *the difference in standard entropies between products and reactants:*

$$\Delta S^\circ_{\text{rxn}} = [cS^\circ(\text{C}) + dS^\circ(\text{D})] - [aS^\circ(\text{A}) + bS^\circ(\text{B})] \qquad (18.6)$$

or, in general, using Σ to represent summation and m and n for the stoichiometric coefficients in the reaction

$$\Delta S^\circ_{\text{rxn}} = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) \qquad (18.7)$$

Third Law of Thermodynamics

- The entropy of a perfect crystal at 0 K is zero.
- The entropy of a substance increases with temperature.