Chemistry, Raymond Chang
10th edition, 2010
McGraw-Hill

Chapter 6
Thermochemistry

Ahmad Aqel Ifseisi
Assistant Professor of Analytical Chemistry
College of Science, Department of Chemistry
King Saud University
P.O. Box 2455 Riyadh 11451 Saudi Arabia
Building: 05, Office: 1A7 & AA53
Tel. 014674198, Fax: 014675992
Web site: http://fac.ksu.edu.sa/aifseisi
E-mail: ahmad3qel@yahoo.com
aifseisi@ksu.edu.sa

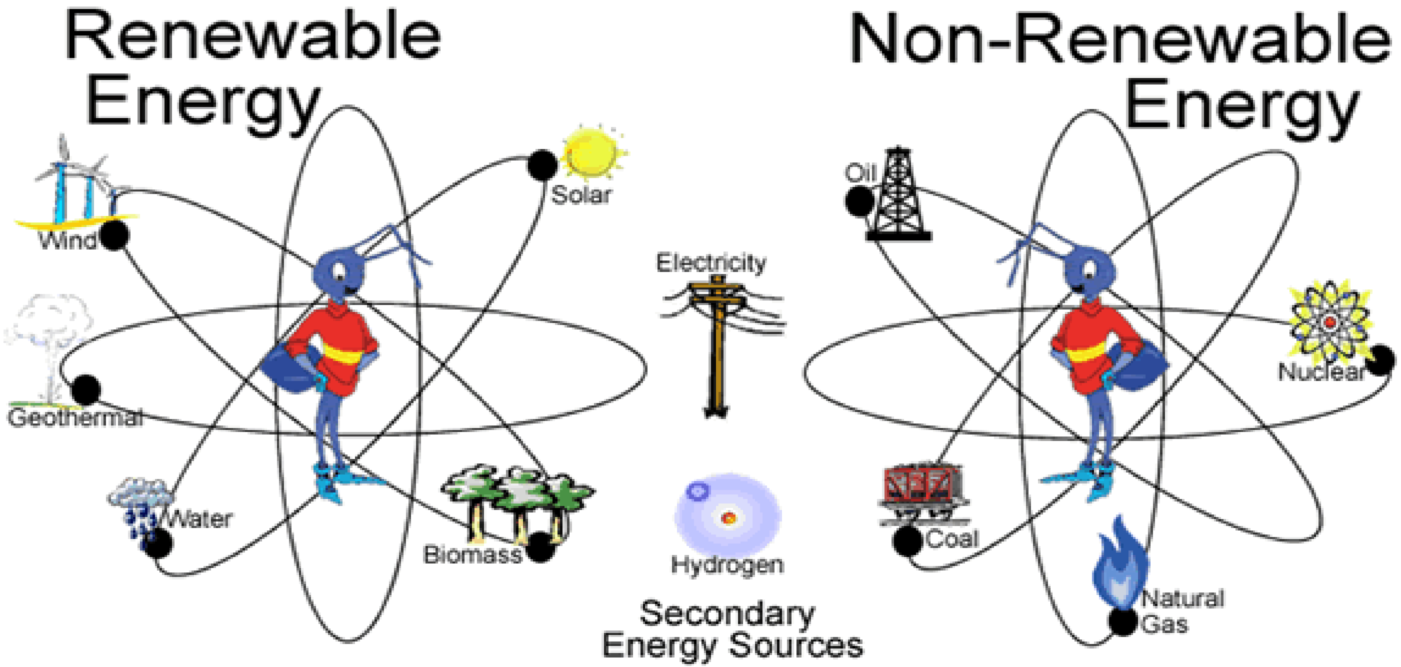
6.1
The nature of energy and types of energy

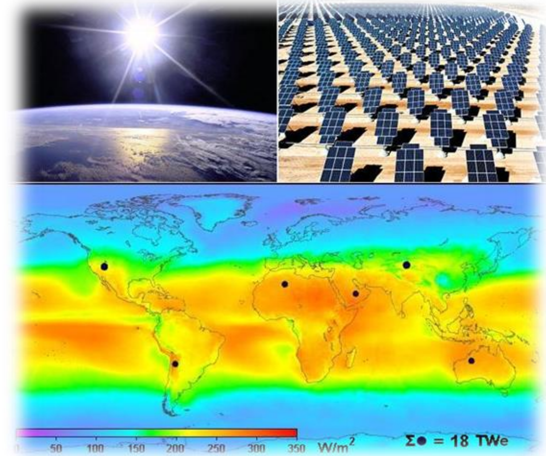
Every chemical reaction obeys two fundamental laws:
- the law of conservation of mass, and
- the law of conservation of energy.

Unlike matter, energy is known and recognized by its effects. It cannot be seen, touched, smelled or weighed.

Energy is usually defined as the capacity to do work.
All forms of energy are capable of doing work (that is, of exerting a force over a distance).

Chemists define work as directed energy change resulting from a process.





Kinetic energy

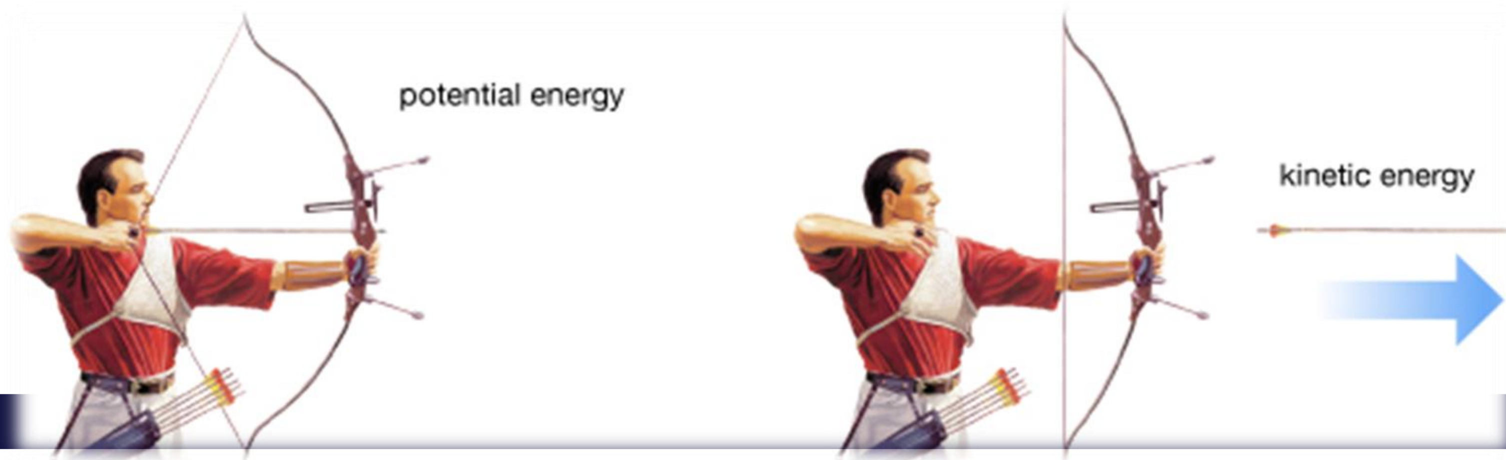
Radiant energy

Thermal energy

Chemical energy

Potential energy

All forms of energy can be converted (at least in principle) from one form to another. When one form of energy disappears, some other form of energy (of equal magnitude) must appear (law of conservation of energy: the total quantity of energy in the universe is assumed constant).



6.2
Energy changes in chemical reactions

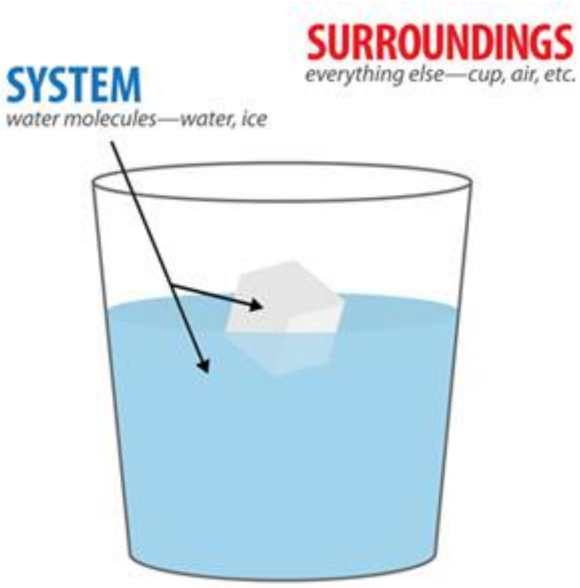
Almost all chemical reactions absorb or produce (release) energy, generally in the form of heat.

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.

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.

*The **system,*** or *the specific part of the universe that is of interest to us.*



The ***surroundings*** are *the rest of the universe outside the system*

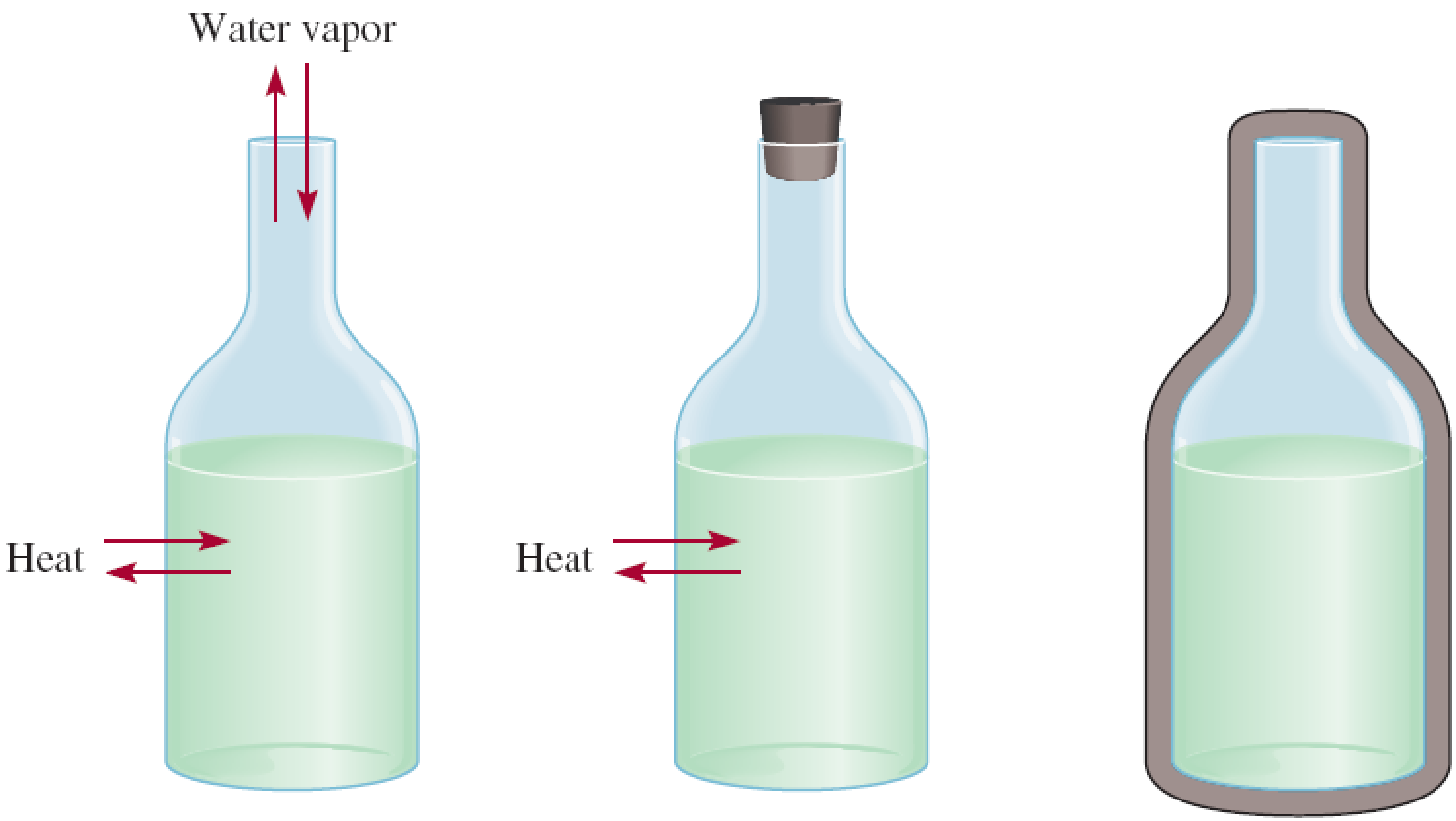
For chemists, systems usually include substances involved in chemical and physical changes.

There are three types of systems;

-An **open system** can exchange mass and energy, usually in the form of heat with its surroundings. e.g., an open system may consist of a quantity of water in an open container.

-If we close the flask, 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.



open system
allows exchange both energy & mass

closed system
allows exchange energy but not mass

isolated system
allows neither energy nor mass to be exchanged

The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + \text{energy}$$

The reacting mixture (H_2, O_2, and H_2O) the system and the rest of the universe the surroundings.

The heat generated by the combustion process is transferred from the system to its surroundings. This reaction is an example of an **exothermic process**, which gives off heat; transfers thermal energy to the surroundings.

The decomposition of mercury(II) oxide (HgO) at high temperatures:

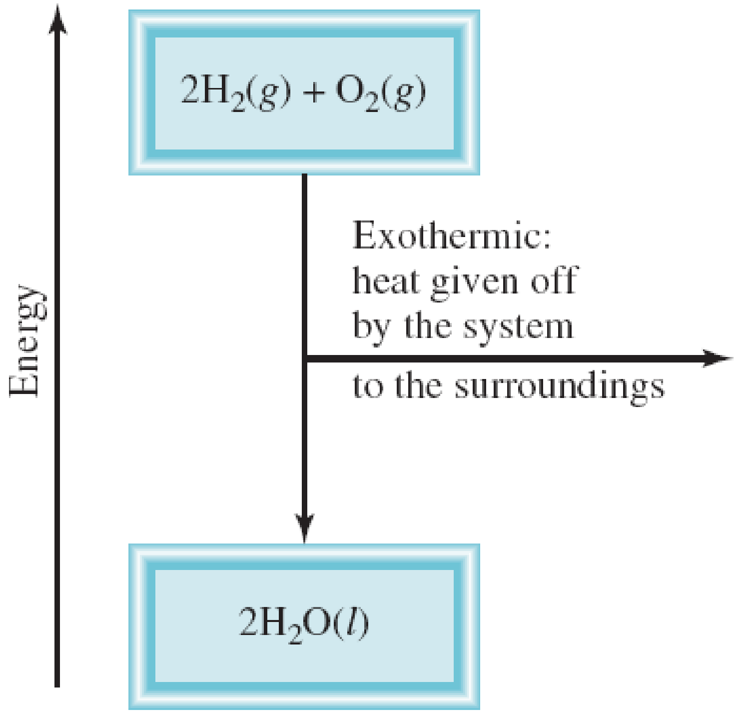
$$\text{energy} + 2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

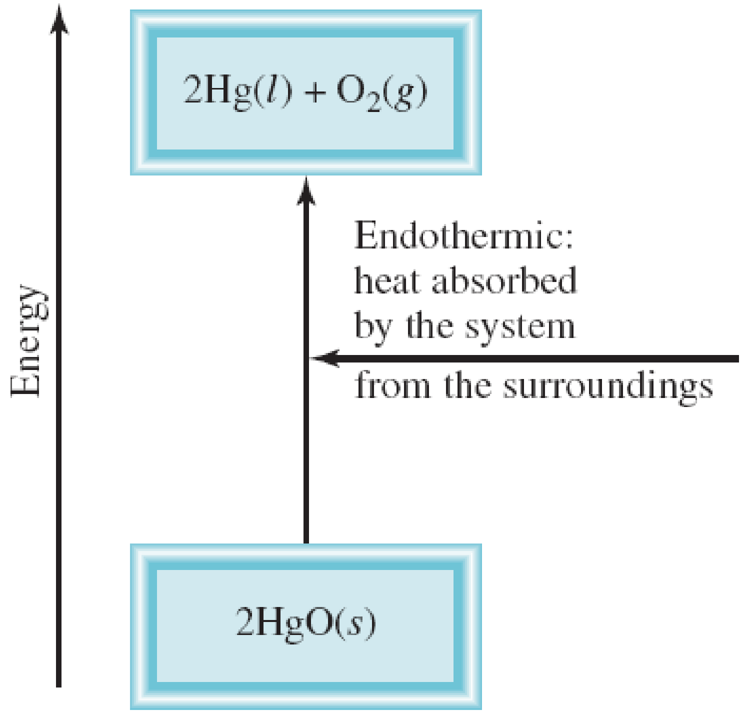
This reaction is an **endothermic process,** in which heat has to be supplied to the system (that is, to HgO) by the surroundings

Exo- comes from the Greek word meaning “outside”; **Endo**- means “within.”.

-In **exothermic** reactions, the total energy of the products is less than the total energy of the reactants. The difference is the heat supplied by the system to the surroundings.

-In **endothermic** reactions, the difference between the energy of the products and the energy of the reactants is equal to the heat supplied to the system by the surroundings.





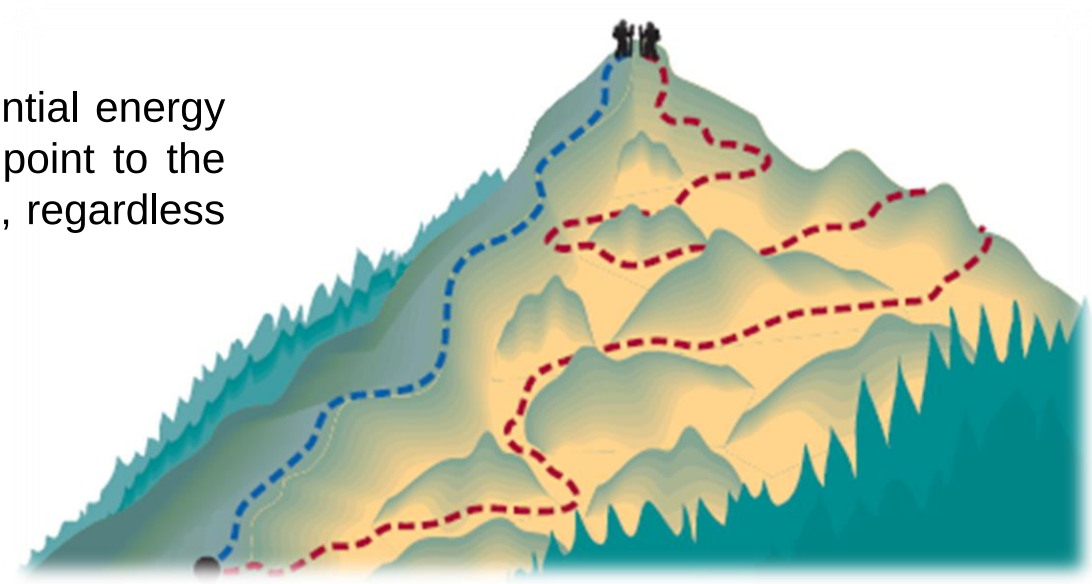
6.3
Introduction to thermodynamics

Thermochemistry is part of a broader subject called **thermodynamics**, which is the scientific study of the interconversion of heat and other kinds of energy.

In thermodynamics, we study changes in the **state of a system**, which is defined by the values of all relevant macroscopic properties, e.g., composition, energy, temperature, pressure and volume. Energy, pressure, volume and temperature are said to be **state functions** — properties that are determined by the state of the system, regardless of how that condition was achieved.

$\Delta V = V_f - V_i$ **where V_i and V_f denote the initial and final volume.**

The net increase in gravitational potential energy when we go from the same starting point to the top of a mountain is always the same, regardless of how we get there.

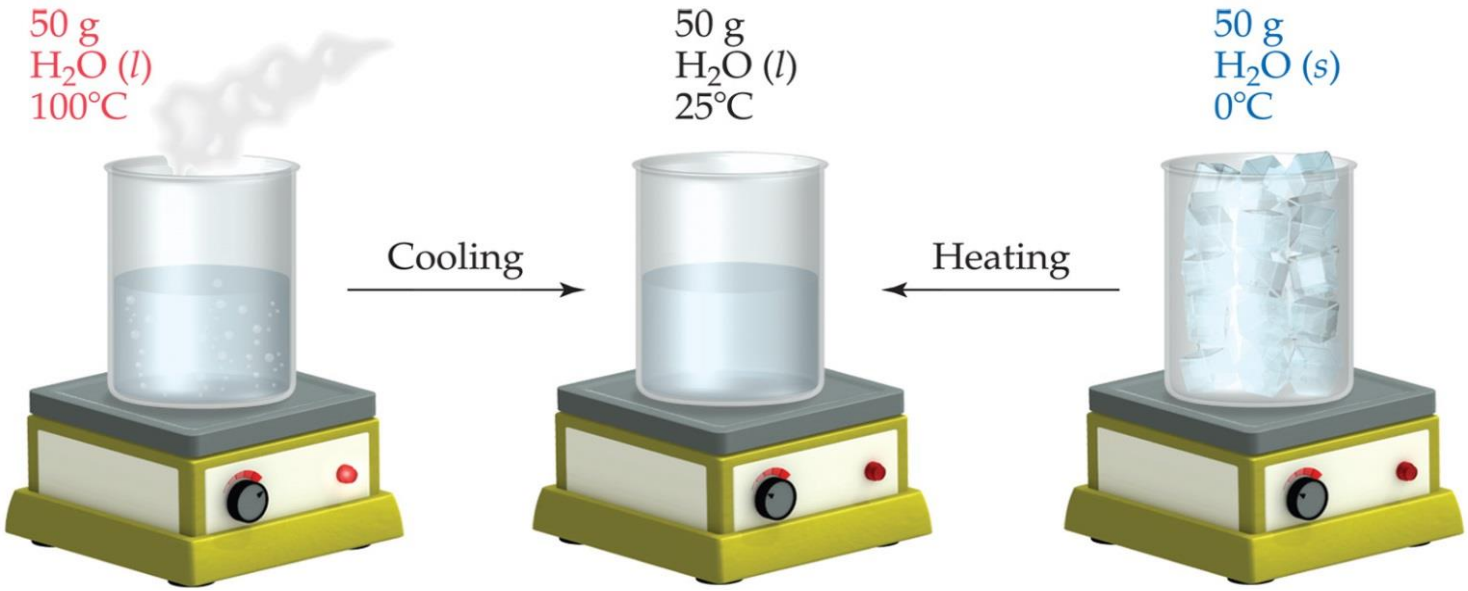


Changes in state functions do not depend on the pathway, but only on the initial and final state.

The water could have reached room temperature from either direction. Therefore, internal energy is a state function. It depends only on the present state of the system, not on the path by which the system arrived at that state.

And so, ΔE **depends only on** E_{initial} **and** E_{final}.

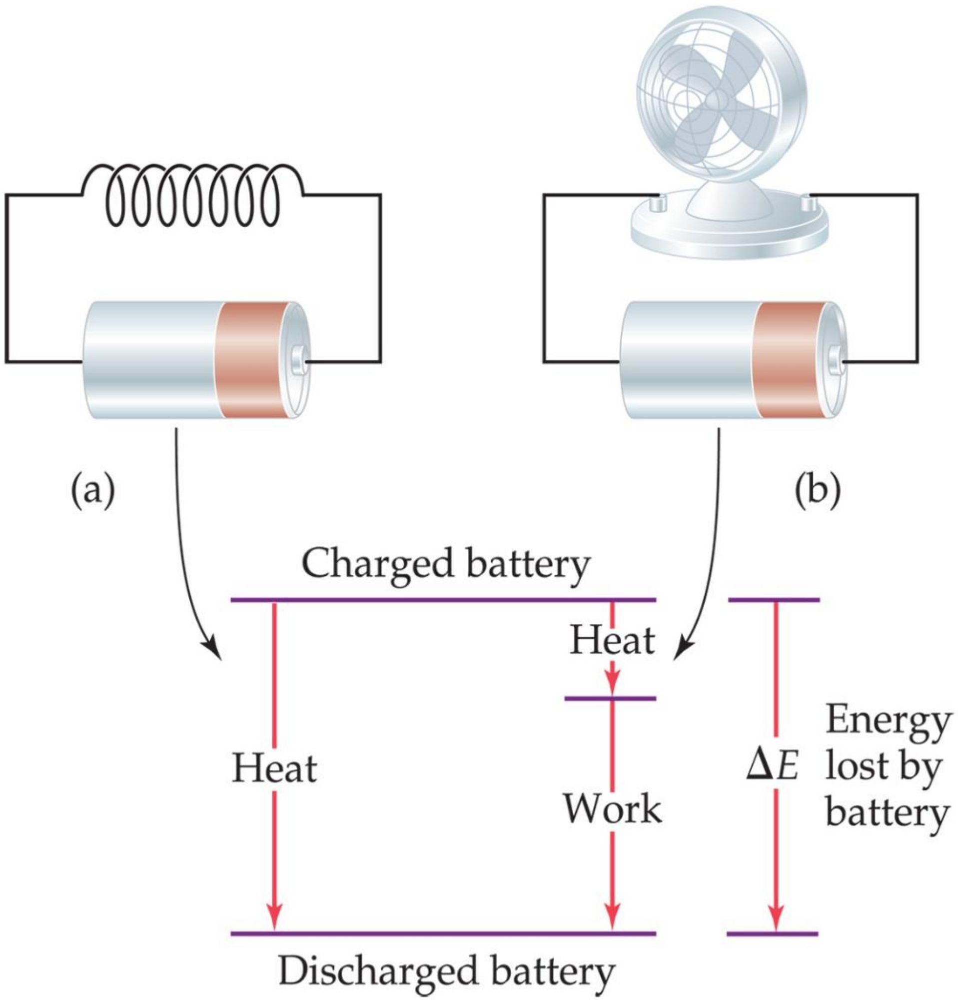
The conditions that influence internal energy include the temperature, pressure and the total quantity of matter in the system because energy in an extensive property.



State function: depends only on the initial and final states of system, not on how the internal energy is used.

However, ***q*** and ***w*** are *not* state functions.

Whether the battery is shorted out or is discharged by running the fan, its ***ΔE*** is the same. But *q* and *w* are different in the two cases.



(a) A battery shorted out by a wire (resistance) loses energy to the surroundings only as heat; no work is performed by the system. (b) A battery discharged through a motor loses energy as work (to make the fan turn) with small amount of heat. w and h are different in two cases but E is same.

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.

-Energy is neither created nor destroyed.

-Energy is conserved.

-The total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.

-Total energy lost by a system equals the total energy gained by a surrounding.

Thermodynamic quantities have three:

(1) a number, and (2) a unit, that together give the magnitude of the change, and (3) a sign that gives the direction.

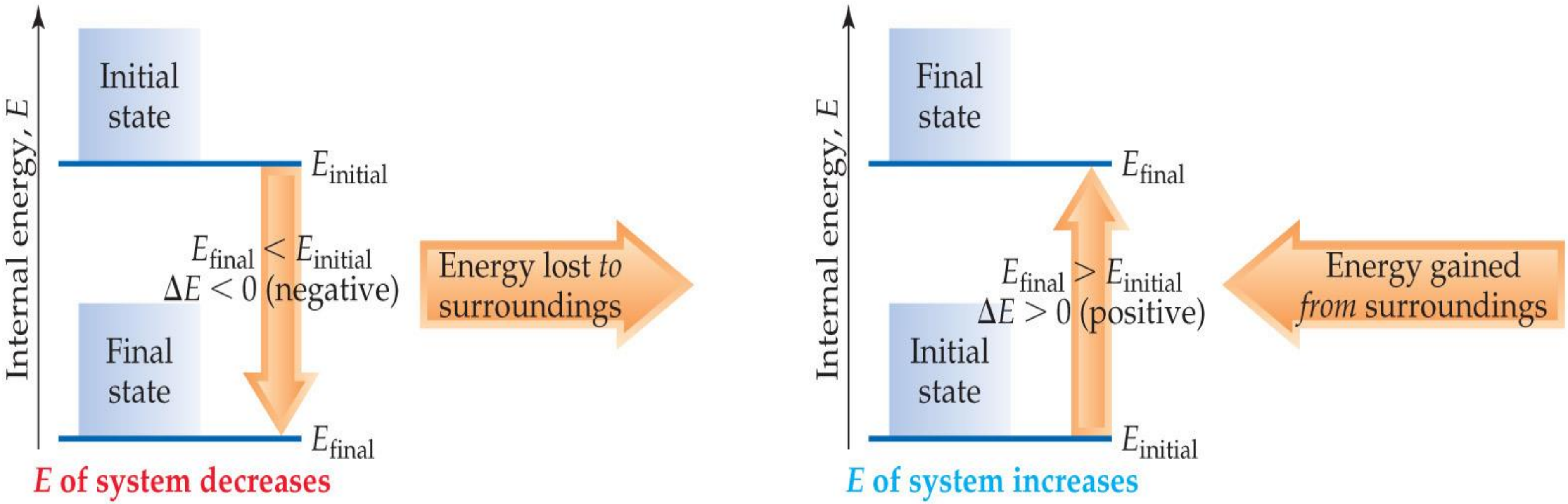
Internal Energy

The internal energy of a system is the sum of all **kinetic** and **potential** energies of all components of the system; we call it ***E***.

Cannot measure **absolute** internal energy.

By definition, the change in internal energy, **Δ*E***, is the final energy of the system minus the initial energy of the system:

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



Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:

$$\mathbf{S(s) + O_2(g) \longrightarrow SO_2(g)}$$

Our system is composed of
- the reactant molecules S and O_2 (the initial state), and
- the product molecules SO_2 (the final state).

We do not know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the change in energy content, Δ**E**, given by

ΔE = E(product) – E(reactants)

= energy content of 1 mol SO_2(g) – energy content of [1 mol S(s) + 1 mol O_2(g)]

We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and Δ**E** is negative.

The transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta E_{sys} + \Delta E_{surr} = 0$$

or

$$\Delta E_{sys} = - \Delta E_{surr}$$

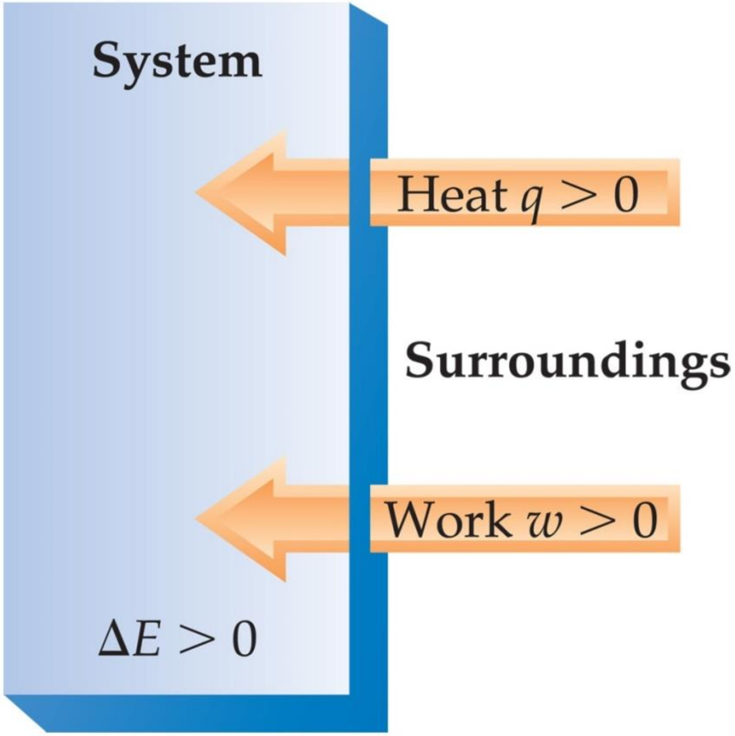
where the subscripts “sys” and “surr” denote system and surroundings, respectively.

When energy is exchanged between the system and the surroundings, it is exchanged as either heat (*q*) or work (*w*).

When a system undergoes any physical or chemical change, the change in internal energy (magnitude and sign) is given by the heat added to or absorbed by the system plus the work done on or by the system:

$$\Delta E = q + w$$

When heat is added to a system or work is done on a system, its internal energy increases.



Heat gained by a system and work done on a system are both +ve quantities. Both increase the internal energy of the system. ***ΔE +ve quantity.***

The sign conventions for *q* and *w* are as follows:

-*q* is +ve for an endothermic process and -ve for an exothermic process,

-*w* is +ve for work done on the system by the surroundings and -ve for work done by the system on the surroundings.

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)	–

ΔE, q, w, and their **Signs**

For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Work

The work can be defined as force ***F*** multiplied by distance ***d***:

$$w = F \times d$$

In thermodynamics, work has a broader meaning that includes;

-Mechanical work (e.g., a crane lifting a steel beam),

-Electrical work (e.g., a battery supplying electrons to light the bulb of a flashlight),

-Surface work (e.g., blowing up a soap bubble).

One way to illustrate mechanical work is to study the expansion or compression of a gas. Many chemical and biological processes involve gas volume changes.

-e.g., when a gas is produced, then the gas produced can be used to push a piston, thus doing work.

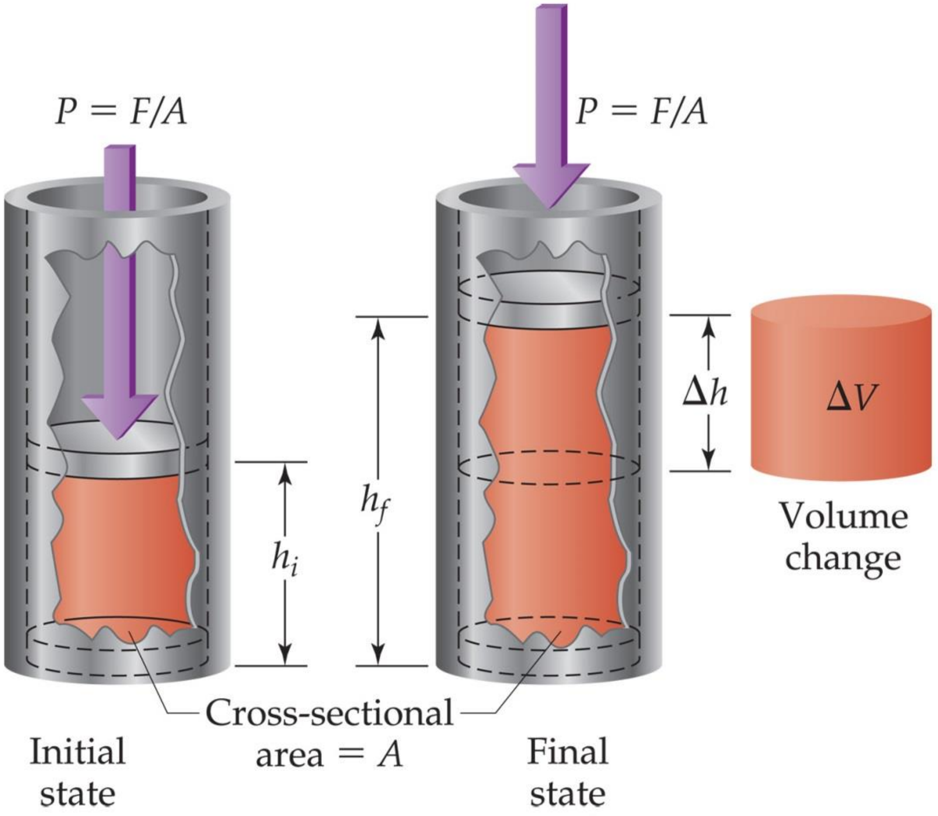
$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

The work performed by the above reaction is called ***pressure-volume* work**. When the pressure is constant, then

$$w = -P\,\Delta V$$

where: P is pressure and ΔV is the change in volume of the system:

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



Why the negative sign in the Equation ???

-For gas expansion (work done *by* the system), $\Delta V > 0$, so $-P\Delta V$ is a -ve quantity.

-For gas compression (work done *on* the system), $\Delta V < 0$, and $-P\Delta V$ is a +ve quantity.

EXAMPLE

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands

(a) against a vacuum and

(b) against a constant pressure of 1.2 atm.

(a) Because the external pressure is zero, no work is done in the expansion.

$w = -P\Delta V$

$= -(0)(6.0 - 2.0)$ L

$= 0$

(b) The external, opposing pressure is 1.2 atm, so

$w = -P\Delta V$

$= -(1.2 \text{ atm})\ (6.0 - 2.0)$ L

$= -4.8$ L·atm

To convert the answer to joules, we write

1 L·atm = 101.3 J

$w = -4.8 \times 101.3 = -4.9 \times 10^2$ J

Practice Exercise

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

$$\Delta E = q + w$$

Heat and work are **not** state functions because they are not properties of a system. They manifest themselves only during a process (during a change). Thus, their values depend on the path of the process and vary accordingly.

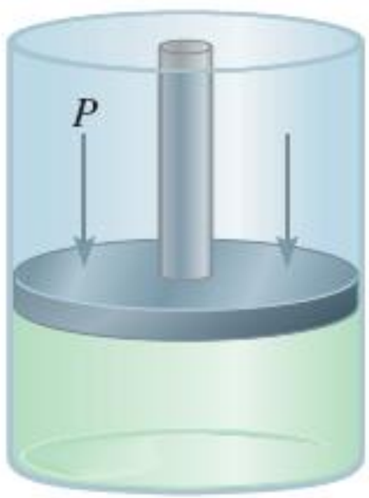
But,,

ΔE is a state function

It is important to note that regardless of which procedure is taken, the change in internal energy of the system, **ΔE**, depends on the sum of (**q + w**). If changing the path from the initial state to the final state increases the value of q, then it will decrease the value of w by the same amount and vice versa, so that **ΔE** remains unchanged.

EXAMPLE

The work done when a gas is compressed in a cylinder like that shown in the Figure is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.



$$\Delta E = q + w$$
$$= -128 \text{ J} + 462 \text{ J}$$
$$= 334 \text{ J}$$

As a result, the energy of the gas increases by 334 J.

Practice Exercise

A gas expands and does *P*-*V* work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

EXAMPLE

Two gases, A and B, are confined in a cylinder-and-piston. Substances A and B react to form a solid product: A(*g*) + B(*g*) → C(*s*). As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Heat is transferred from the system to the surroundings, and work is done on the system by the surroundings, so q is negative and w is positive: q = –1150 J and w = 480 kJ. Thus,

$$\Delta E = q + w = (-1150\ \text{J}) + (480\ \text{J}) = -670\ \text{J}$$

The negative value of ΔE tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.


Thank You!