Chapter 2. The First Law

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The basic concepts

2.1 Work 功, heat 熱, and energy 能量
2.2 The internal energy 內能
2.3 Expansion work 膨脹功
2.4 Heat transactions
2.5 Enthalpy 焓
2.6 Adiabatic changes 絕熱變化

Thermochemistry 熱化學

2.7 Standard enthalpy changes
2.8 Standard enthalpies of formation
2.9 The temperature-dependence of reaction enthalpies
State functions 状態函數 and exact differentials

2.10 Exact and inexact differentials
2.11 Changes in internal energy
2.12 The Joule-Thomson effect
Basic concepts of thermodynamics

- Use the principle of conservation of energy — the experimental observation that energy can be neither created nor destroyed — to assess the energy changes that accompany physical and chemical processes.
- The means by which a system can exchange energy with its surroundings in terms of the work it may do or the heat that it may produce.
- The target concept is enthalpy, very useful for keeping track of the heat output (or requirements) of physical processes and chemical reactions at constant pressure.
- How to establish relations between different properties of a system. A property can be measured indirectly by measuring others and then combining their values.
- Liquefaction of gases; establish the relation between the heat capacities of a substance under different conditions.
Chapter 2. Introduction

• The release of energy can be used to provide heat when a fuel burns in a furnace, to produce mechanical work when a fuel burns in an engine, and to generate electrical work when a chemical reaction pumps electrons through a circuit.

• In chemistry, we encounter reactions that can be harnessed to provide heat and work, reactions that liberate energy which is squandered (often to the detriment of the environment) but which give products we require, and reactions that constitute the processes of life.

• Thermodynamics, the study of the transformations of energy, enables us to discuss all these matters quantitatively and to make useful predictions.
The **system** is the part of the world in which we have a special interest, e.g., a reaction vessel, an engine, an electrochemical cell, a biological cell, etc.

The **surroundings** comprise the region outside the system and are where we make our measurements.

**Fig. 2.1** (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.
2.1 Work, heat, and energy

- **Work** is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. e.g., the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

- **The energy** of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.
An **exothermic process** is a process that releases energy as heat into its surroundings, combustion;

An **endothermic process** is a process in which energy is acquired from its surroundings as heat.

**Fig. 2.2** (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.
Molecular interpretation 2.1 Heat

Heating is the transfer of energy that makes use of *disorderly molecular motion* called *thermal motion*. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings.

**Fig. 2.3** When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.
Work is the transfer of energy that makes use of organized motion. The atoms in a spring move in an orderly way when wound; the electrons in an electric current flow in an orderly direction. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way.

**Fig. 2.4** When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.
2.2 The internal energy

- The total energy of a system is called its **internal energy**, \( U \). The internal energy is the total kinetic and potential energy of the molecules in the system. We denote by \( \Delta U \) the change in internal energy when a system changes from an initial state \( i \) with internal energy \( U_i \) to a final state \( f \) of internal energy \( U_f \):  

\[
\Delta U = U_f - U_i
\]

1 J = 1 kg m\(^2\) s\(^{-2}\)

1 cal = 4.184 J exactly

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C.
**Molecular interpretation 2.2 The internal energy of a gas**

The kinetic energy an atom of mass \( m \) as it moves through space is:

\[
E_K = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2
\]

\[
U_m = U_m(0) + \frac{3}{2}RT
\]

The equipartition theorem: for a collection of particles at thermal equilibrium at a temperature \( T \), the average value of each quadratic contribution to the energy is the same and equal to \( \frac{1}{2}kT \)

\[
U_m = U_m(0) + \frac{5}{2}RT \quad \text{(linear molecule, translation and rotation only)}
\]

\[
U_m = U_m(0) + 3RT \quad \text{(nonlinear molecule, translation and rotation only)}
\]

*Fig. 2.5* The rotational modes of molecules and the corresponding average energies at a temperature \( T \). (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.
The **First Law of thermodynamics**: The internal energy of an isolated system is constant.

\[ \Delta U = q + w \]

### 2.3 Expansion work: the work arising from a change in volume.

\[ dU = dq + dw \]

(a) The general expression for work

\[ dw = -Fdz \]

\[ w = - \int_{V_i}^{V_f} p_{ex} dV \]
(b) **Free expansion**: expansion against zero opposing force.

\[ p_{\text{ex}} = 0. \]

**Table 2.1** Varieties of work*

<table>
<thead>
<tr>
<th>Type of work</th>
<th>( dw )</th>
<th>Comments</th>
<th>Units†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion</td>
<td>(-p_{\text{ex}} dV)</td>
<td>( p_{\text{ex}} ) is the external pressure ( dV ) is the change in volume</td>
<td>Pa ( m^3 )</td>
</tr>
<tr>
<td>Surface expansion</td>
<td>( \gamma d\sigma )</td>
<td>( \gamma ) is the surface tension ( d\sigma ) is the change in area</td>
<td>N ( m^{-1} ) ( m^2 )</td>
</tr>
<tr>
<td>Extension</td>
<td>( fdl )</td>
<td>( f ) is the tension ( dl ) is the change in length</td>
<td>N ( m )</td>
</tr>
<tr>
<td>Electrical</td>
<td>( \phi dQ )</td>
<td>( \phi ) is the electric potential ( dQ ) is the change in charge</td>
<td>V ( C )</td>
</tr>
</tbody>
</table>

* In general, the work done on a system can be expressed in the form \( dw = -Fdz \), where \( F \) is a ‘generalized force’ and \( dz \) is a ‘generalized displacement’.
† For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.
2.3 Expansion work
(c) Expansion against constant pressure

\[ w = -p_{ex} \int_{V_i}^{V_f} \, dV = -p_{ex} (V_f - V_i) \]

If we write the change in volume as \( \Delta V = V_f - V_i \),

\[ w = -p_{ex} \Delta V \]

**Fig. 2.7** The work done by a gas when it expands against a constant external pressure, \( p_{ex} \), is equal to the shaded area in this example of an indicator diagram.
Comment 2.2

Integral:

\[ f(x) = x^2 \]

\[ \int_{1}^{3} x^2 \, dx = \left( \frac{1}{3} x^3 + \text{constant} \right) \bigg|_{1}^{3} \]

\[ = \frac{1}{3} (3^3 - 1^3) = \frac{26}{3} \approx 8.67 \]
(d) Reversible expansion

- **Reversible change**: a change that can be reversed by an *infinitesimal* modification of a variable.

- A system is in *equilibrium* with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. e.g., the thermal equilibrium of two systems with the same temperature.

\[
dw = -p_{ex} \, dV = -p \, dV
\]

\[
w = - \int_{V_i}^{V_f} p \, dV
\]
(e) Isothermal reversible expansion

The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Perfect gas

\[ w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \]

**Fig. 2.8** The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm \( p = nRT/V \). The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.
Example 2.1 Calculating the work of gas production

• Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

• **Answer:** (a) $w = 0$
• Fe(s) + 2 HCl(aq) $\rightarrow$ FeCl$_2$(aq) + H$_2$(g)
• (b) $w = -p_{ex}\Delta V$. $\Delta V = V_f - V_i \approx V_f = \frac{nRT}{p_{ex}}$, $n$ the amount of H$_2$.

• Fe 55.85 g mol$^{-1}$

• The external pressure?

• **Self Test 2.1** Calculate the expansion work when 50 g of water is electrolyzed under constant pressure at 25°C?

• **Correct Answer:** ($-10$ kJ) 2H$_2$O(l) $\rightarrow$ O$_2$(g) + 2H$_2$(g)
2.4 Heat transactions

• Generally change in internal energy of a system

\[ dU = dq + dw_{\text{exp}} + dw_e \]

where \( dw_e \) is work in addition to the expansion work, \( dw_{\text{exp}} \)

\[ dU = dq \quad \text{(at constant volume, no additional work)} \]

For a measurable change,

\[ \Delta U = q_V \]
Calorimetry is the study of heat transfer during physical and chemical processes. A calorimeter is a device for measuring energy transferred as heat. The most common device for measuring $\Delta U$ is an adiabatic bomb calorimeter.

*Fig. 2.9* A constant-volume bomb calorimeter. The ‘bomb’ is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.
2.4 Heat transactions (a) Calorimetry

- The change in temperature, $\Delta T$, of the calorimeter is proportional to the heat that the reaction releases or absorbs. Therefore, by measuring $\Delta T$ we can determine $q_V$ and hence find $\Delta U$. The conversion of $\Delta T$ to $q_V$ is best achieved by calibrating the calorimeter using a process of known energy output and determining the calorimeter constant, the constant $C$ in the relation

$$q = C\Delta T$$
2.4 Heat transactions (a) Calorimetry

\[ q = IVt \]

Illustration 2.2 The calibration of a calorimeter

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from above eqn the energy supplied as heat is

\[ q = (10.0 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = 3.6 \times 10^4 \text{ A V s} = 36 \text{ kJ} \]

because 1 A V s = 1 J. If the observed rise in temperature is 5.5 K, then the calorimeter constant is \( C = (36 \text{ kJ})/(5.5 \text{ K}) = 6.5 \text{ kJ K}^{-1} \).
(b) The **heat capacity at constant volume**

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v \]

**Fig. 2.10** The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.
The partial derivative, for example, if \( z(x,y) = x^2y \), then

\[
\left( \frac{\partial z}{\partial x} \right)_y = \left( \frac{\partial [x^2y]}{\partial x} \right)_y = y \frac{dx^2}{dx} = 2yx
\]

**Fig. 2.11** The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to \( T \). The slope of this curve at any point is the partial derivative \( (\partial U/\partial T)_V \).
Heat capacity

- **Illustration 2.3 Estimating a constant-volume heat capacity**

- The heat capacity of a monatomic perfect gas can be calculated from the internal energy:
  
  \[ U_m = U_m(0) + \frac{3}{2}RT, \text{ so from } C_v = \left( \frac{\partial U}{\partial T} \right)_V \]

- \[ C_{v,m} = \frac{\partial}{\partial T} \left( U_m(0) + \frac{3}{2}RT \right) = \frac{3}{2}R \]

- The numerical value is 12.47 J K\(^{-1}\) mol\(^{-1}\)

\[ dU = C_v dT \quad \text{(at constant volume)} \]

\[ \Delta U = C_v \Delta T \quad \text{(at constant volume)} \quad q_V = C_v \Delta T \]