The Second and Third Laws of Thermodynamics: Entropy

Recommended books

1. P. W. Atkins and J. D. Paula: *Physical Chemistry (10th edition)*
2. Ira N. Levine: *Physical Chemistry (6th edition)*
3. M. Mahbubul Huque and M. Yousuf Ali Mollah: *Principles of Physical Chemistry*

Lecture-1

Contents

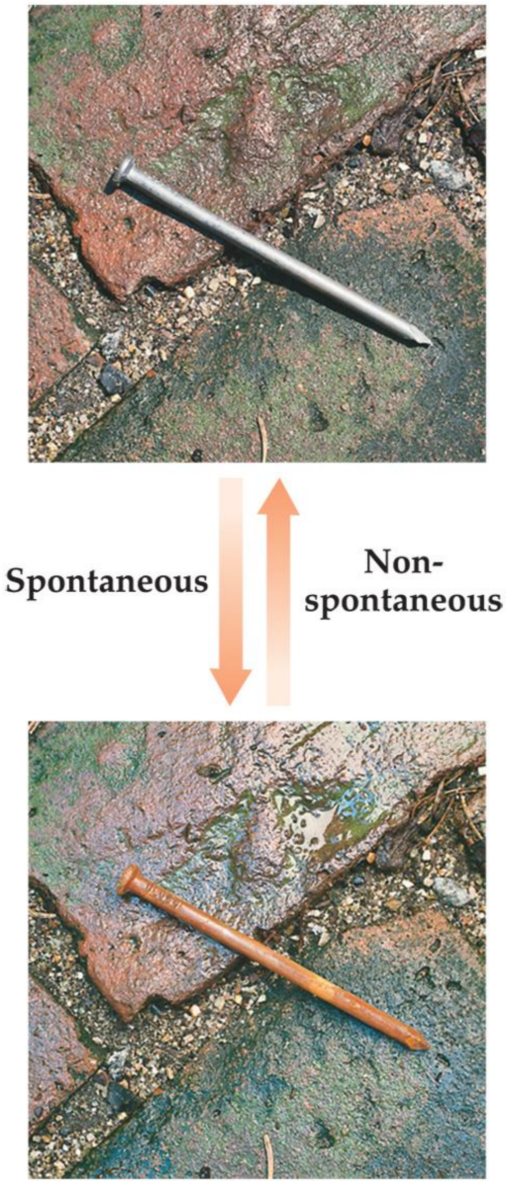
- Chapter contents and Learning Outcomes (LOs)
- Spontaneous and non-spontaneous processes
- Necessity of the Second Law of Thermodynamics
- Second Law of Thermodynamics
- The Direction of Spontaneous Changes

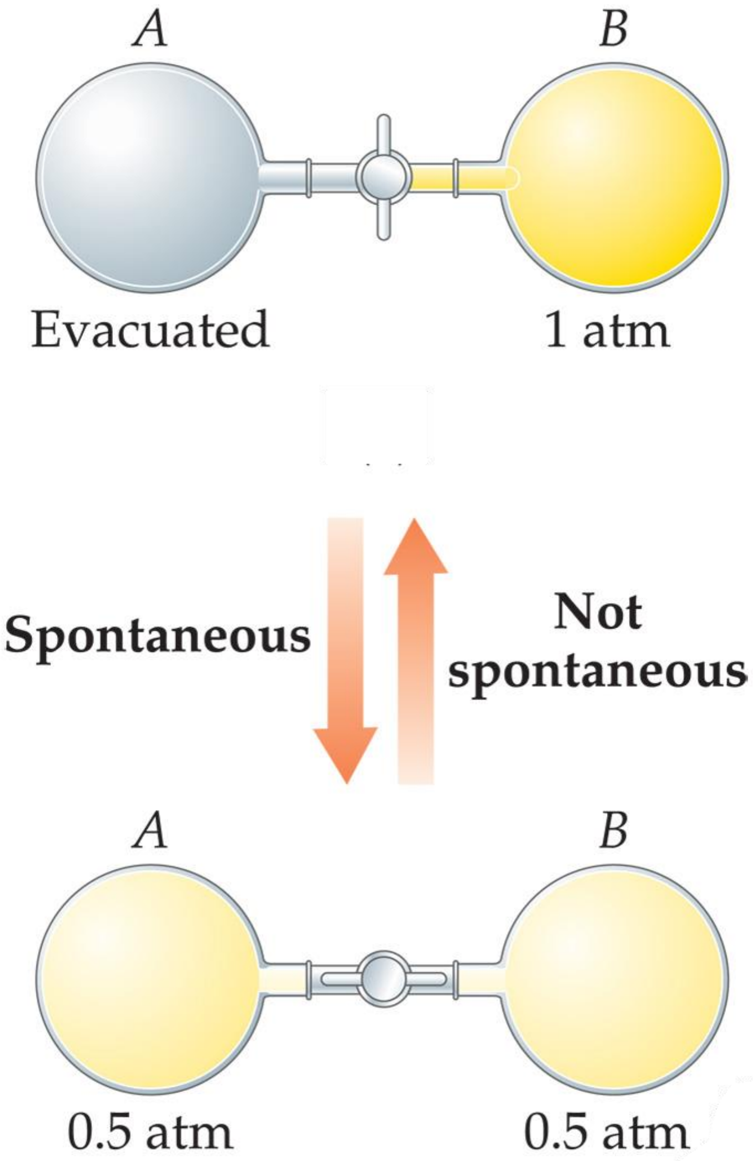
The Second and Third Laws of Thermodynamics (10 lectures): Necessities; spontaneous and nonspontaneous processes; second law; heat engine, Carnot cycle, entropy and change of entropy in different processes; nature of entropy; entropy and universe; Nernst heat theorem, third law, absolute and conventional entropy, statistical view of entropy, residual entropy.

Students should be able to:

a) Comprehend the need for second law
b) State second law of thermodynamics in different ways
c) Describe Carnot cycle and Carnot theorem
d) Appreciate the concept of entropy
e) Apprise yourself about entropy changes in reversible and irreversible processes
f) Compute entropy changes for ideal gas under different conditions
g) Derive entropy change using Boltzmann probability equation
h) Know the physical significance of entropy
i) Calculate entropy change on mixing of ideal gas
j) Predict entropy change associated with different physical and chemical changes
k) Know the Nernst heat theorem
l) State third law thermodynamics in different form
m) Use third law of thermodynamics in calculating absolute entropies
n) Test the validity of the third law of thermodynamics
o) Calculate and interpret residual entropy

Spontaneous and Non-spontaneous Processes

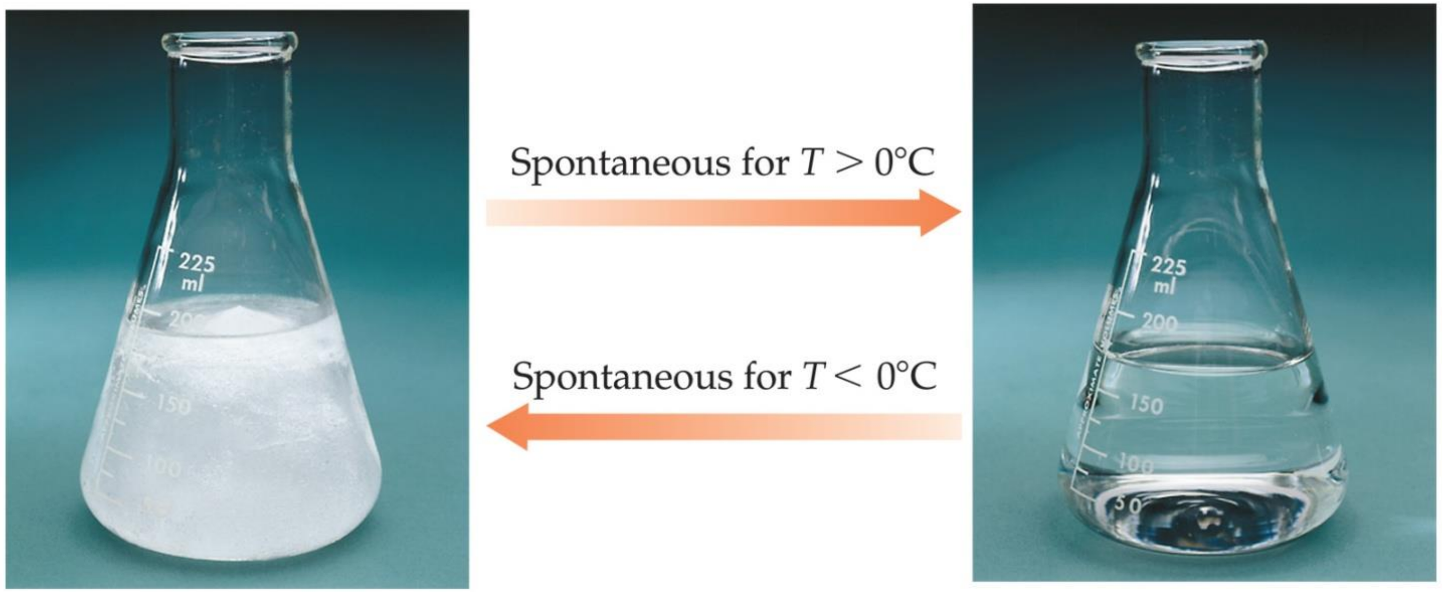




Spontaneous and Non-spontaneous Processes

- Processes that are spontaneous at one temperature may be non-spontaneous at other temperatures.

Above 0°C it is spontaneous for ice to melt. Below 0°C the reverse process is spontaneous.



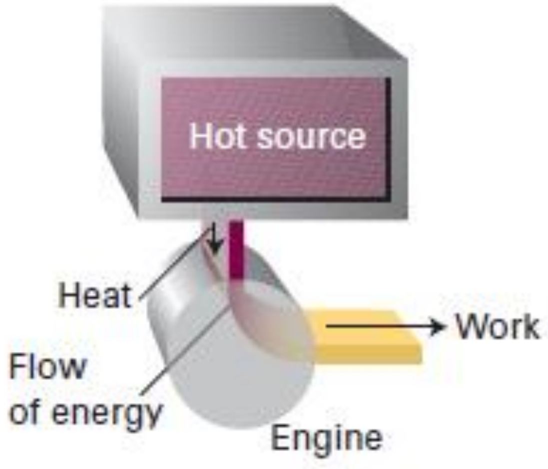
Necessity of the **Second Law of thermodynamics.**

- A major application of thermodynamics to chemistry is to provide information about equilibrium in chemical systems.
- The first law cannot say what the final equilibrium concentrations will be.
- The second law provides such information. The second law leads to the existence of the state function entropy S, which possesses the property that for an isolated system the equilibrium position corresponds to maximum entropy.

Second Law of Thermodynamics

Clausius statement : Heat cannot flow spontaneously from a cooler to a hotter object if nothing else happens.

Kelvin Statement: It is impossible for a system to undergo a cyclic process in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.



Impossible

It has proved impossible to construct an engine like that shown in the figure, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

The Direction of Spontaneous Change

- What determines the direction of spontaneous change?
- Is it the energy of the *system that tends towards a minimum?*

Two arguments show that this cannot be so.

✓First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so.

✓Secondly, if the energy of a system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount (by the First Law). The increase in energy of the surroundings is just as spontaneous a process as the decrease in energy of the system.

The Direction of Spontaneous Change

Spontaneous changes are always accompanied by a dispersal of energy.

During a spontaneous change in an isolated system the total energy is dispersed into random thermal motion of the particles in the system.

Consider a ball (the system) bouncing on a floor (the surroundings).

- On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses.
- The reverse has never been observed to take place on a macroscopic scale.

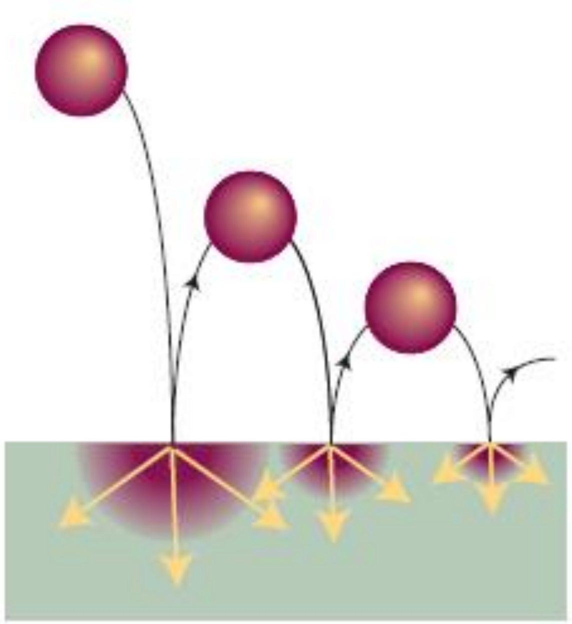


Figure. The direction of spontaneous change for a ball bouncing on a floor.

The Direction of Spontaneous Change

The molecular interpretation of the irreversibility expressed by the Second Law.

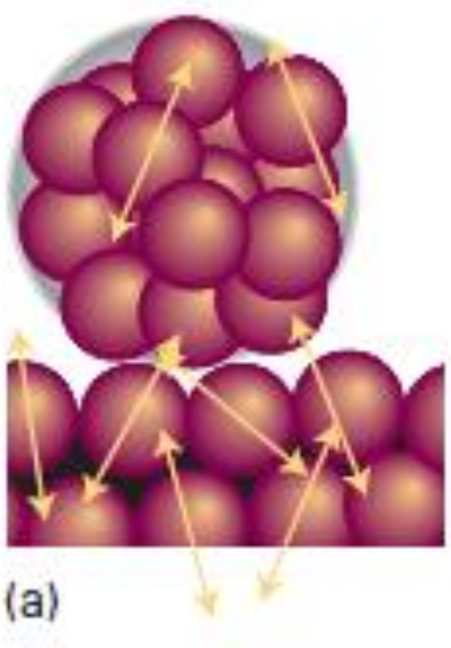


Figure (a). A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows.

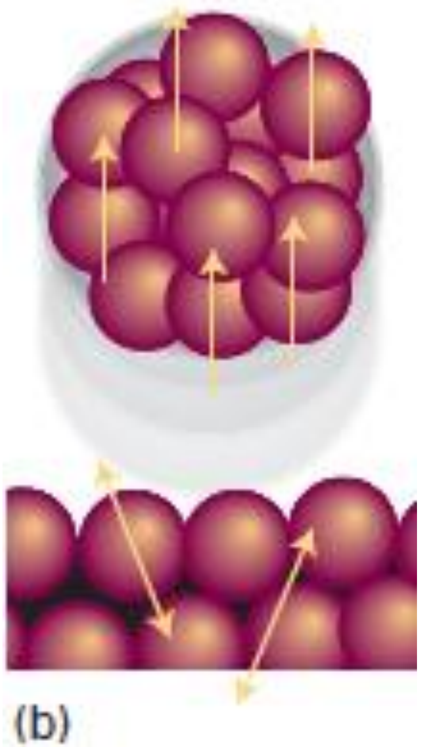


Figure (b). For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is **highly improbable.**

Entropy

The First Law uses the **internal energy** to identify **permissible changes**.

Only those changes may occur for which the internal energy of an isolated system remains constant.

The Second Law uses the **entropy** to identify the spontaneous changes among those **permissible changes**.

The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{tot} > 0$$

Lecture-2

Contents

- Entropy
- Calculation of entropy change in
    - cyclic process
    - reversible adiabatic process
    - reversible phase change
    - reversible isothermal process

Thermodynamic definition of entropy

$$dS = \frac{dq_{\text{rev}}}{T}$$

where q_{rev} is the heat supplied reversibly.

For a measurable change between two states i and f

$$\Delta S = \int_{\text{i}}^{\text{f}} \frac{\mathrm{d}q_{\text{rev}}}{T}$$

Calculation of entropy change

- Find a **reversible path** between them
- Integrate the energy supplied as heat at each stage of the path
- Divide by the temperature at which heating occurs.

1. Cyclic process

Since S is a state function, $\Delta S = 0$ for every cyclic process.

2. Reversible adiabatic process

Here $dq_{\text{rev}} = 0$; therefore

$\Delta S = 0$ rev. ad. proc.

3. Reversible phase change at constant *T* and *P*

At constant *T*,

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int_1^2 dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

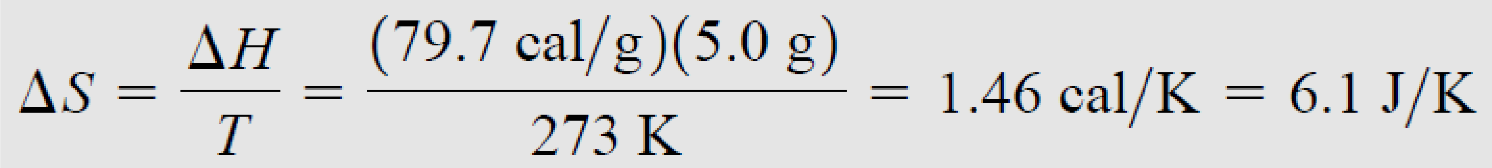
At constant *P*, $q_{\text{rev}} = q_P = \Delta H$

$$\Delta S = \frac{\Delta H}{T}$$

Example

Find ΔS for the melting of 5.0 g of ice (heat of fusion 79.7 cal/g) at 0°C and 1 atm. Find ΔS for the reverse process.

The melting is reversible and therefore



$$\Delta S = \frac{\Delta H}{T} = \frac{(79.7\ \text{cal/g})(5.0\ \text{g})}{273\ \text{K}} = 1.46\ \text{cal/K} = 6.1\ \text{J/K}$$

For the freezing of 5.0 g of liquid water at 0°C and 1 atm, q_{rev} is negative, and ΔS = -6.1 J/K.

Exercise

The heat of vaporization of water at 100°C is 40.66 kJ/mol. Find ΔS when 5.00 g of water vapor condenses to liquid at 100°C and 1 atm. (*Answer:* -30.2 J/K.)

4. Reversible isothermal process

Here *T* is constant,

and $\Delta S = \int_1^2 T^{-1}\, dq_{\text{rev}} = T^{-1} \int_1^2 dq_{\text{rev}} = q_{\text{rev}}/T.$

Thus $\Delta S = q_{\text{rev}}/T$ rev. isotherm. proc.

Examples

A reversible phase change (case 3 in this list) and two of the four steps of a Carnot cycle.