# Chapter 21 Entropy and Second Law of Thermodynamics

The first law of thermodynamics is a statement of the conservation of energy. Yet several processes consistent with the first law *do not* occur in nature. Why?

Heat always flows from a hot body to a cold body, never in the reverse direction. Why?

All the nature processes mentioned above proceed *only in one direction*; we never see the reversed order of events.

Such seemingly trivial observations form the basis of the second law of thermodynamics.

The second law tells us something about *how natural processes evolve*.

# History of Thermodynamics (II)

The development of the steam energy motivates the industrial revolution and also stimulates Carnot to devise an ideal thermodynamic cycle of operation.

The steam engine has to operate between two heat reservoirs whose "levels" are determined by the temperatures. In Carnot's view it was the fall of *caloric* from the hot to the cold reservoir that led to the work output.

Despite this *incorrect* notion that heat is a conserved substance, Carnot formulated important theorems that laid the foundation for the subsequent development of thermodynamics.

The initial formulations of the second of thermodynamics were in terms of the efficiencies of heat engines.

# 21.1 Heat Engines and The Kelvin-Planck Statement of The Second Law (I)

A *heat engine* is a device that converts heat into mechanical work. Examples include steam engines, gasoline engines, and diesel engines.

*Repetitive cycle of processes*: An engine has some "working substance" that is returned to its initial state at the end of each cycle.

Figure 21.2 is a schematic representation of a heat engine that operates between a hot reservoir at temperature  $T_H$  and a cold reservoir at temperature  $T_c$ .



# 21.1 Heat Engines and The Kelvin-Planck Statement of The Second Law (II)

It is convenient in the following discussion to include the sign of the heat transfer *explicitly*.

In one complete cycle, the engine returns to its initial state, so the internal energy of the working substance does not change.

$$\Delta U = Q - W = 0$$

The net work done by the engine in a cyclic process is equal to the net heat influx:

$$W = |Q_H| - |Q_C|$$



## 21.1 Heat Engines and The Kelvin-Planck Statement of The Second Law (III)

The thermal efficiency  $\varepsilon$  of a heat engine is defined as the work output divided by the heat input ( $W_{output}/Q_{input}$ ):

$$\varepsilon = \frac{W}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

A gasoline engine has an efficiency of about 20%, whereas for a diesel engine it is about 30%.

#### The Kelvin-Planck statement

It is impossible for a heat engine that operates in a cycle to convert its heat input completely into work.



## 21.2 Refrigerators and The Clausius Statement of The Second Law

The Clausius statement of the second law

It is impossible for a cyclical device to transfer heat continuously from a cold body to a hot body without the input work or other effect on the environment.

The coefficient of performance (COP) of a **refrigerator** 

$$COP = \frac{|Q_C|}{W}$$

What happens when the outside temperature is higher than the inside? Heat pump.





# 21.3 Equivalence of the Kelvin-Planck and Clausius Statements (I)



# 21.3 Equivalence of the Kelvin-Planck and Clausius Statements (II)



# 21.4 Reversible and Irreversible

In a **Quasistatic** process the state variables of a system change infinitely slowly so that the system is always arbitrarily close to thermal equilibrium.

Provided the process takes much longer than the so called relaxation time, the process is effectively quasistatic.

In a **resersible** process the system may also be made to retrace its thermodynamic path back to the initial state. Three conditions must be satisfied:1. quasistatic, 2. no friction, 3. infinitesimal thermal equilibrium.

Any process that does not satisfy these conditions is **irreversible**.

### 21.5 The Carnot Cycle

In 1824, Carnot devised a reversible cycle of operations that is a useful ideal.

It may involve any electrical, magnetic, or chemical cycle. Here we assume the working substance is an ideal gas.

The Carnot cycle consists of two isothermal and two adiabatic processes.



10

### Efficiency of the Carnot Cycle

$$|Q_H| = \int_a^b P dV = nRT_H \ln\left(\frac{V_b}{V_a}\right)$$
$$|Q_C| = \int_d^c P dV = nRT_C \ln\left(\frac{V_c}{V_d}\right)$$

For an adiabatic proces  $\mathcal{B}V^{\gamma} = \text{constant}$   $\therefore TV^{\gamma-1} = \text{constant}$ 

$$\begin{cases} T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1} \\ T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1} \end{cases} \Longrightarrow \begin{cases} \frac{V_b}{V_a} = \frac{V_c}{V_d} \end{cases}$$

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \implies \varepsilon_C = 1 - \frac{T_C}{T_H} \quad \text{Carnot efficiency}$$

11

### Carnot's Theorem

- (i) All reversible engines operating between two given reservoirs have the same efficiency.
- (ii) No cyclical heat engine has a greater efficiency than a reversible engine operating between the same two temperature.



# 21.6 The Gasoline Engine (Otto Cycle)

The gasoline engine is the most common example of a heat engine.

Its four-stroke cycle was devised in 1876 by Rochas, whereas Otto developed and built the first prototype in 1876.



### The Gasoline Engine (Otto Cycle) (II)

The **Otto cycle** actually consists of six steps, but only four "strokes" involve motion of the piston.

The six steps in the idealized Otto cycle:

Intake stroke (O to A), Compression stoke (A to B), Ignition (B to C), Power stroke (C-D), Exhaust (D to A), Exhaust stroke (A to O)



### Example 21.2

Calculate the efficiency of the (idealized) Otto cycle.

Solution:

Heat input  $|Q_{in}| = nC_v(T_C - T_B)$ Heat output  $|Q_{out}| = nC_v(T_D - T_A)$ Net work  $W = |Q_{in}| - |Q_{out}|$ So the efficiency

$$\varepsilon = \frac{W}{|Q_{in}|} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

For the adiabatic processes A to B and C to D,

we use  $TV^{\gamma-1} = const$ . Since  $V_A = V_D$  and  $V_B = V_C$ 

$$\varepsilon = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \frac{T_D}{T_C} = 1 - (\frac{V_C}{V_D})^{\gamma - 1} = 1 - \frac{1}{r^{\gamma - 1}}$$

#### The Efficiency of Otto Cycle (III)

The efficiency of the idealized Otto cycle is  $\varepsilon = 1 - \frac{T_D}{T_C} = 1 - \frac{1}{r^{\gamma - 1}}$ 

Where  $r=V_1/V_2$  is called the compression ratio. The efficiency increase with the compression ratio. However, if the compression ratio is too high, the temperature and pressure of the gas after the compression stroke become high enough for the gas to ignite spontaneously. This premature ignition, which is heard as a knock or ping, is damaging to the engine.

\*the operation of a real engine involves irreversible processes, friction, heat loss, and a change in the working fluid because of the combustion of the fuel. Thus the efficiency is much less than the ideal cycle of 56%. A value around 20% is attained.

### Otto Cycle and Diesel Cycle (IV)

Why the efficiency of Otto cycle is less than that of Carnot cycle?

$$\varepsilon_O = 1 - \frac{T_D}{T_C} < \varepsilon_C = 1 - \frac{T_A}{T_C}$$
, since  $T_D > T_A$ 

**Diesel cycle** employs a much higher compression ratio of 15. The air is first compressed by itself so that its temperature rises. The fuel, which is injected only after the compression, ignites spontaneously. There is no problem of preignition.

The efficiency of the diesel engines is higher ( $\approx 25\%$ ) than gasoline engines, and they burn a less refined. However, they are difficult to start in cold weather.

### 21.7 Entropy

Oth law: identification of temperature as a state variable.

1st law: the concept of internal energy.

2nd law: another state function "entropy".

The introduction of entropy *broadens* the scope of the second law of thermodynamics from heat engines to the evolution of nature processes.

We will introduce the concept of entropy by means of the Carnot cycle.

### 21.7 Entropy: Carnot Cycle

For a Carnot cycle  $\frac{|Q_H|}{T_H} - \frac{|Q_C|}{T_C} = 0$  or  $\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$ 

An arbitrary reversible cycle may approximate it by a series of Carnot cycles.



In the infinitely limit, we have

$$\oint \frac{dQ_R}{T} = 0$$

19

#### Entropy as a State Function

Consider two equilibrium states *a* and *b*. In the infinitely limit, we have

$$\underbrace{\int_{a}^{b} \frac{dQ_{R}}{T}}_{(\mathrm{I})} = \underbrace{\int_{a}^{b} \frac{dQ_{R}}{T}}_{(\mathrm{II})}$$



This integral is independent of the path between the equilibrium states. In the present context we define an infinitesimal change in entropy as

$$ds = \frac{dQ_R}{T}$$

The change in entropy depends only on the initial and final equilibrium states, not on the thermodynamic path.

#### Entropy: (a) Reversible Process of an Ideal Gas

$$dQ = dU + dW$$
  

$$dU = nC_v dT$$
  

$$dW = PdV = (nRT/V)dV$$
  

$$\frac{dQ}{T} = \frac{nC_v dT}{T} + \frac{nRdV}{V}$$
  

$$\Delta S = nC_v \ln(\frac{T_f}{T_i}) + nR\ln(\frac{V_f}{V_i})$$

Since S is a state function, the expression for  $\Delta S$  may be used even for an irreversible process involving an ideal gas between the same initial and final equilibrium states.

21

#### Entropy: (b) Adiabatic Free Expansion of an Ideal Gas

Since the temperature of an adiabatic free expansion gas does not change, *a suitable replacement* would be a quasistatic isothermal expansion, i.e.  $T_{f=}T_{i}$ .

$$\Delta S = nR\ln(\frac{V_f}{V_i})$$

There is no heat exchanged with the environment  $\Delta Q=0$  and the internal energy is the same  $\Delta U=0$ . Why the entropy of the system still increase in this condition?

### Example 21.5

A Copper ball of mass m=0.5 kg and specific heat  $c=390J/kg\cdot K$  is at a temperature T1=90 °C. The ball is thrown into a large lake at T2=10 °C, which stays constant. Find the change in entropy of (a) the ball, (b) the lake, and (c) the universe.

Solution:

(a) temperature changes from 363 °K to 283 °K

$$\Delta S_B = \int_{T_1}^{T_2} mc \, \frac{dT}{T} = mc \ln(\frac{T_2}{T_1}) = -48.5 \text{ J/K}$$

(b) the change in entrop of the lake is

$$\Delta S_{L} = \frac{\Delta Q}{T_{2}} = \frac{\int_{T_{1}}^{T_{2}} mcdT}{T_{2}} = 55.1 \text{ J/K}$$

(c) The entropy change of the universe is

$$\Delta S_U = \Delta S_B + \Delta S_L = 6.6 \text{ J/K}$$

21.8 Entropy and The Second Law

Another formulation of the second law of the thermodynamics:

 $\Delta S \ge 0$ 

In a reversible process the entropy of an isolated system stays constant; in an irreversible process the entropy increases.

Clausius introduced the entropy function to help distinguish between **reversible** and **irreversible** process.

The principle of increase of entropy is connected with the transition of a system from **ordered** to **disordered** states.

This in turn leads to a relation between **entropy** and **probability**.

### 21.9 The Availability of Energy

All forms of energy can be fully converted from one form to another, e.g. kinetic energy and potential energy. However, this symmetry breaks when dealing with heat. Internal energy cannot be completely converted to other forms or fully used to do work.

The availability of energy can be summarized as follows:

- 1. The degradation of energy is associated with the transition of the system from an ordered to a disordered state.
- 2. In any natural (irreversible) process, some energy becomes unavailable to do useful work.

### 21.10 Entropy and Disorder

The second law says that an isolated system tends to evolve toward states of higher entropy. This leads us to identify entropy as a measure of disorder in a system.

A highly ordered state has low entropy, whereas a disordered state has high entropy.

The principle of increase in entropy, often called "time's arrow", tells us how the natural (irreversible) process always evolves toward states of higher entropy.

# **Exercises and Problems**

Ch.21: Ex. 7, 18, 21, 22, 29, 30 Prob. 1, 3, 4, 7, 10, 11