

Homework: 42, 44, 46, 54, 56, 78 (p. 533-535)

42. What is the internal energy of 2.0 mol of an ideal monatomic gas at 273 K?

$$E = nC_V T$$

$$C_V = \frac{3}{2} R = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E = 2.0 \times 12.5 \times 273 = 6825 \text{ (J)}$$

$$E \approx 6.8 \text{ (kJ)}$$

The change in internal energy of the gas:

$$\Delta E_{\text{int}} = \frac{3}{2} nR\Delta T = \frac{3}{2} nRT_2 - \frac{3}{2} nRT_1 = \frac{3}{2} (378,75 - 252,5) = 189,375 \text{ (J)}$$

$f=5 \leftarrow$ diatomic gas : $C_V = \frac{5}{2} R$

46. Under constant pressure, the temperature of 3.0 mol of an ideal monatomic gas is raised 15.0 K. What are (a) the work W done by the gas, (b) the energy transferred as heat Q , (c) the change ΔE_{int} of the gas, and (d) the change ΔK in the average KE per atom?

(a) At constant pressure:

$$W = p\Delta V = nR\Delta T = 3.0 \times 8.31 \times 15.0 \approx 374 \text{ (J)}$$

(b)

$$Q = nC_p\Delta T = n \times \frac{5}{2} R \times \Delta T = \frac{5}{2} W \approx 935 \text{ (J)}$$

(c) We use the first law of thermodynamics:

$$\Delta E_{\text{int}} = Q - W \quad (\text{or } \Delta E_{\text{int}} = nC_V\Delta T = \frac{3}{2}nR\Delta T)$$

$$\Delta E_{\text{int}} = 935 - 374 = 561 \text{ (J)}$$

(d) For a monatomic gas: $K_{\text{avg}} = \frac{3}{2}kT \Rightarrow \Delta K_{\text{avg}} = \frac{3}{2}k\Delta T$

$$\Delta K_{\text{avg}} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 15.0 \approx 3.1 \times 10^{-22} \text{ (J)}$$

1.38×10^{-23}
 $3 \times N_A$
 $\times \Delta K$
 of Sample

$$C_p = C_v + R$$

$$C_v = \frac{3}{2}R$$

54. We know that for an **adiabatic process** $pV^\gamma = \text{constant}$. Evaluate "constant" for an **adiabatic process** involving exactly 2.0 **mol** of an ideal gas passing through the state having exactly **p**=1.5 atm and **T**=300 K. Assume a **diatomic gas** whose molecules rotate but do not oscillate.

$$1 \text{ atm} = 1.01 \times 10^5 \text{ (Pa)} \rightarrow \text{N/m}^2$$

Equation of state:

$$pV = nRT$$

$$V = \frac{nRT}{p} = \frac{2.0 \times 8.31 \times 300}{1.5 \times 1.01 \times 10^5} \approx 0.033 \text{ (m}^3\text{)}$$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{\frac{f}{2}R + R}{\frac{f}{2}R}$$

$f \rightarrow f=5$

For a diatomic gas, **f=5**:

$$\gamma = \frac{7}{5}$$

$$\text{constant} = pV^\gamma = 1.5 \times 1.01 \times 10^5 \times 0.033^{\frac{7}{5}} = 1.28 \times 10^3 \text{ (N/m}^2 \times \text{(m}^3\text{)}^{1.4}\text{)}$$

$$\text{constant} = 1.28 \times 10^3 \text{ (N m}^{2.2}\text{)} \leftarrow \text{unit}$$

56. Suppose 1.0L of a gas with $\gamma=1.30$, initially at 285 K and 1.0 atm, is suddenly compressed adiabatically to half its initial volume. Find its final (a) pressure and (b) temperature. (c) If the gas is then cooled to 273 K at constant pressure, what is its final volume?

$$\Rightarrow p_i V_i^\gamma = p_f V_f^\gamma; \quad V_f = \frac{1}{2} V_i$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1}$$

$$pV = nRT, \quad p = \text{constant} \Rightarrow \frac{V'_f}{V_f} = \frac{T'_f}{T_f}$$

273

78. (a) An ideal gas initially at pressure p_0 undergoes a free expansion until its volume is 3.0 times its initial volume. What then is the ratio of its pressure to p_0 ? (b) The gas is next slowly and adiabatically compressed back to its original volume. The pressure after compression is $(3.0)^{1/3} p_0$. Is the gas monatomic, diatomic, or polyatomic? (c) What is the ratio of the average kinetic energy per molecule in this final state to that in the initial state?

$$(a) \quad p_0 V_0 = p_1 V_1; V_1 = 3V_0 \Rightarrow p_1 = \frac{1}{3} p_0 \quad \frac{p_0 V_0}{p_1} = 3 \quad \frac{p_1 V_1}{p_0}$$

$$(b) \quad p_1 V_1^\gamma = p'_1 V_0^\gamma$$

$$p'_1 = p_1 \left(\frac{V_1}{V_0} \right)^\gamma = \frac{1}{3} p_0 3^\gamma = 3^{\gamma-1} p_0 = 3^{1/3} p_0$$

$$\Rightarrow \gamma - 1 = \frac{1}{3} \Rightarrow \gamma = \frac{4}{3} = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{\frac{f}{2} + 1}{\frac{f}{2}} = \frac{f+2}{f}$$

$$f = 6 : \text{polyatomic}$$

(c)

$$K_{avg} = \frac{3}{2} kT$$

$$PV = nRT$$

$$\Rightarrow T = \frac{PV}{nR}$$

ratio

$$r = \frac{K'_{avg}}{K_{avg}} = \frac{T'_1}{T_0}$$

$$r = \frac{T'_1}{T_0} = \frac{p'_1 V'_1}{p_0 V_0} = \frac{p'_1}{p_0} \xrightarrow{3^{1/3} p_0} = 3^{1/3} = \underline{1.44} \text{ (since } V'_1 = V_0 \text{)}$$

adiabatic expansion

$$P_0 V_0 T_0 \xrightarrow{\text{adiabatic expansion}} P_1 V_1 T_1 \xrightarrow{\text{adiabatic expansion}} P_2 V_2 T_2$$
$$P_0 V_0 = P_1 V_1$$
$$T_0 = T_1$$
$$V_1 = 3 V_0$$
$$P_1 V_1^\gamma = P_2 V_2^\gamma$$
$$P_2 = 3^{1/3} P_0$$

Chapter 4 Entropy and the Second Law of Thermodynamics

4.1. Reversible, Irreversible Processes and Entropy

4.2. The Second Law of Thermodynamics

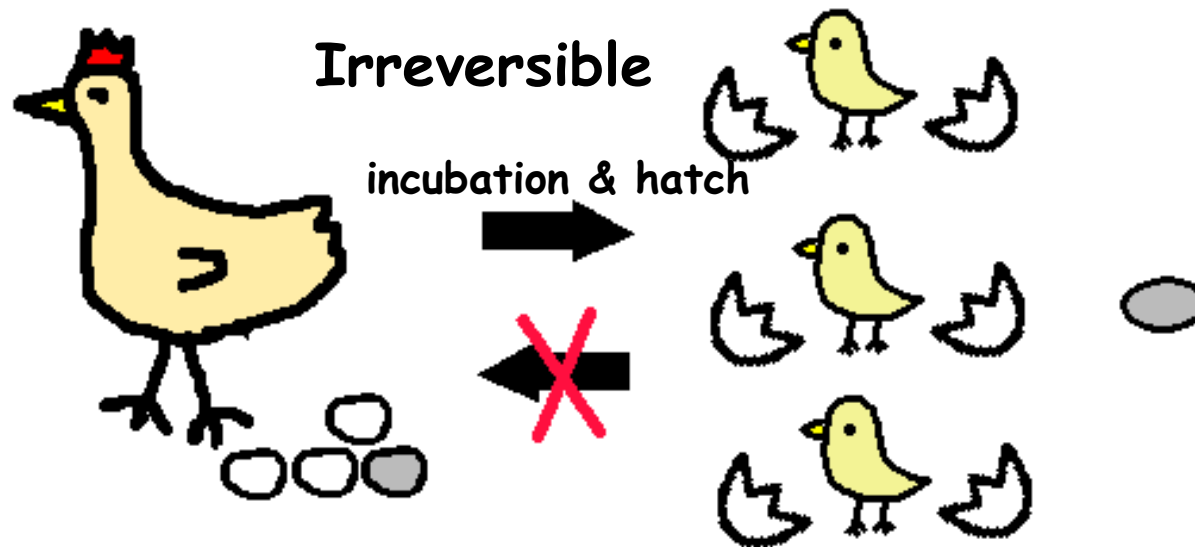
4.3. Entropy in the Real World: Engines

4.4. A Statistical View of Entropy

What is Physics?

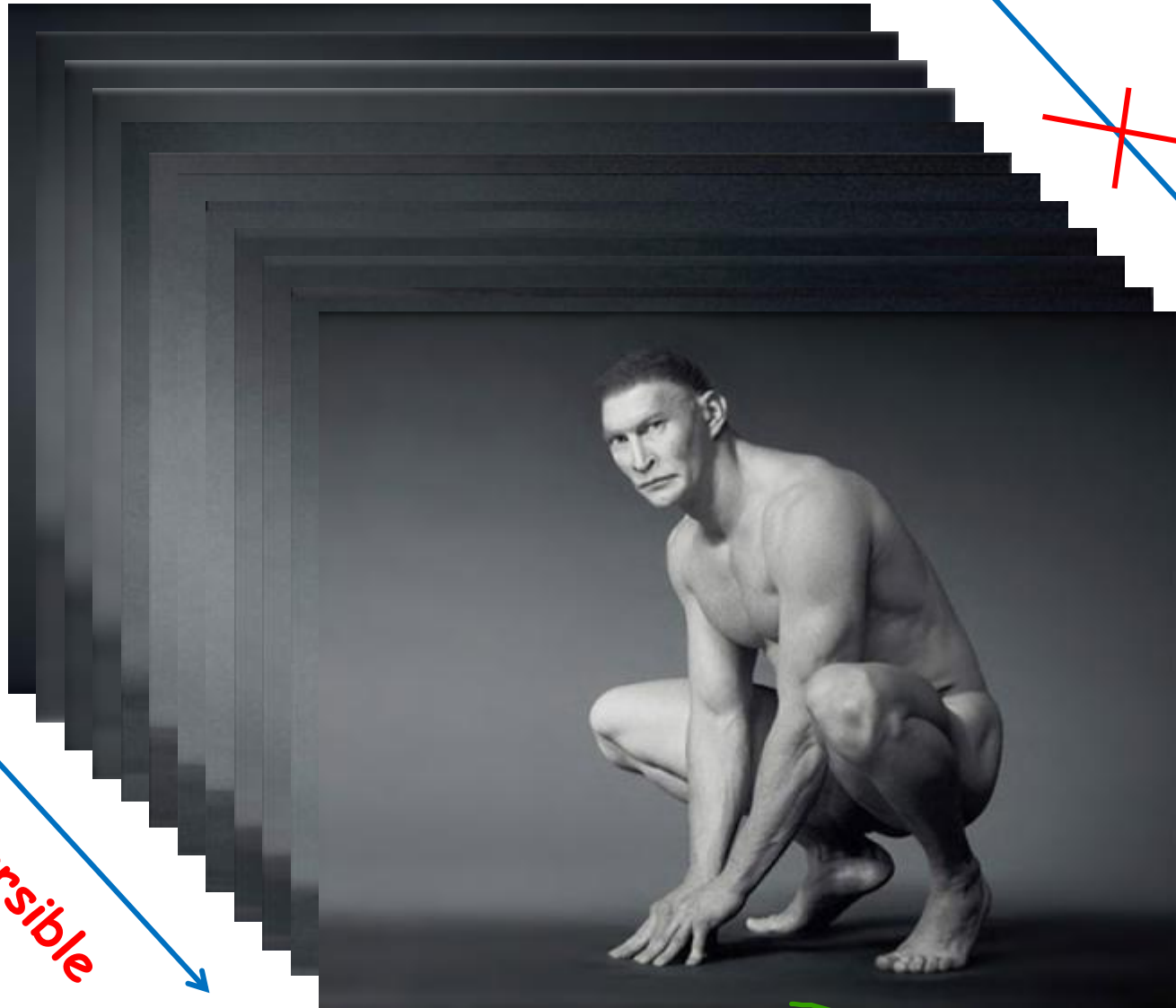
- Time has direction, from the past to the future
- One-way processes that can occur only in a certain sequence and never in the reverse sequence are **irreversible**, meaning that they can not be reversed.

Examples: a pizza is baked, water flows from high level to low level, current moves from high potential to low potential, etc.



Evolution

Irreversible



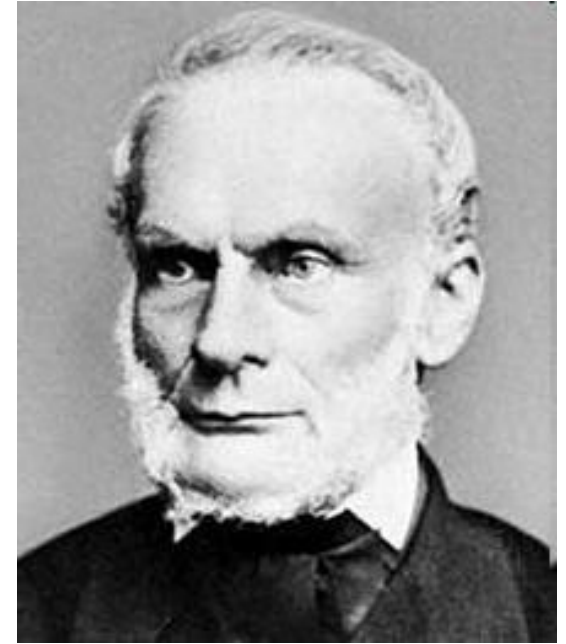
Credit:
Daniel Lee

- In this chapter, we study why one-way processes are irreversible
- The key to understand why one-way processes cannot be reversed involves a quantity known as Entropy

What is Entropy?

Entropy is the extensive property of the system (depends on the mass of the system) and its unit of measurement is J/K . Entropy is heat or energy change per degree Kelvin temperature.

Entropy is denoted by ' S '.



Clausius - author of the entropy concept

Interdisciplinary applications of entropy

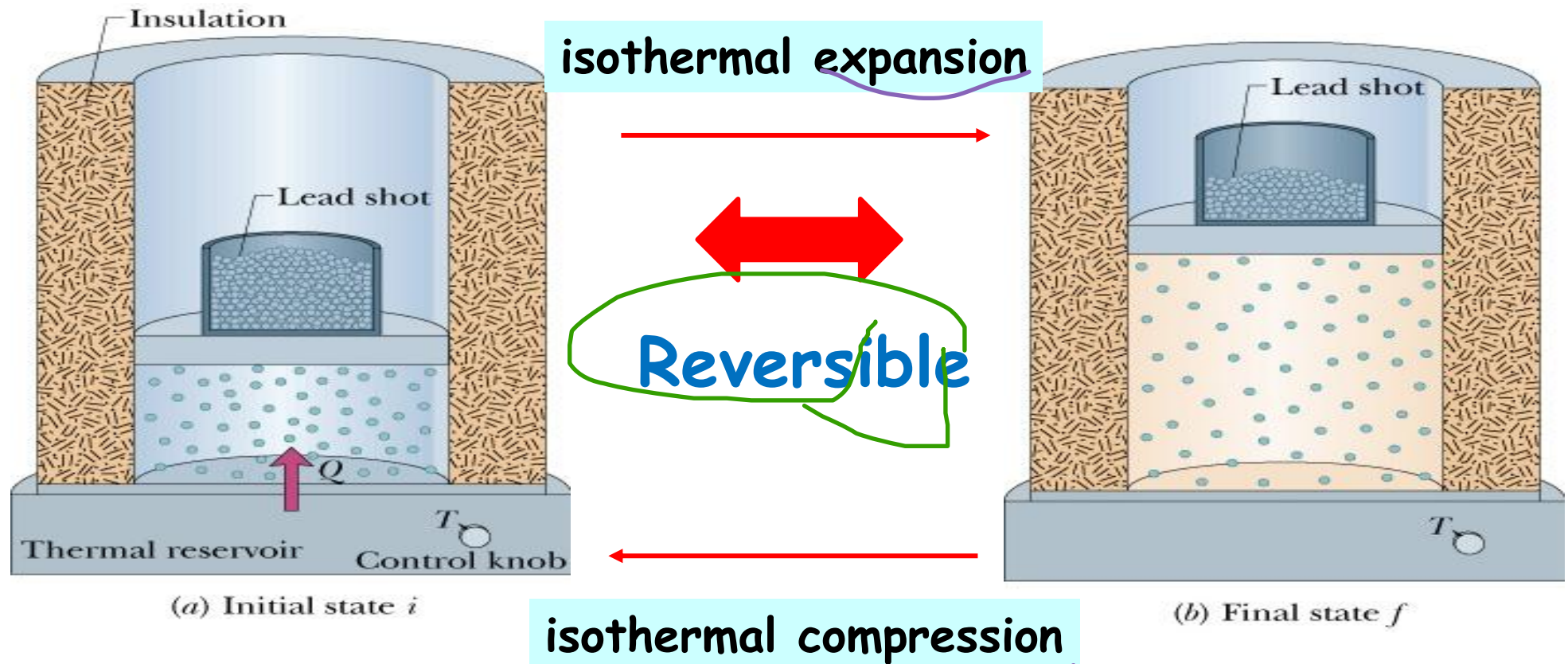
Although the concept of entropy was originally a thermodynamic construct, it has been adapted in the other following fields of study:

- ✓ information theory
- ✓ psychodynamics
- ✓ thermoeconomics
- ✓ evolution

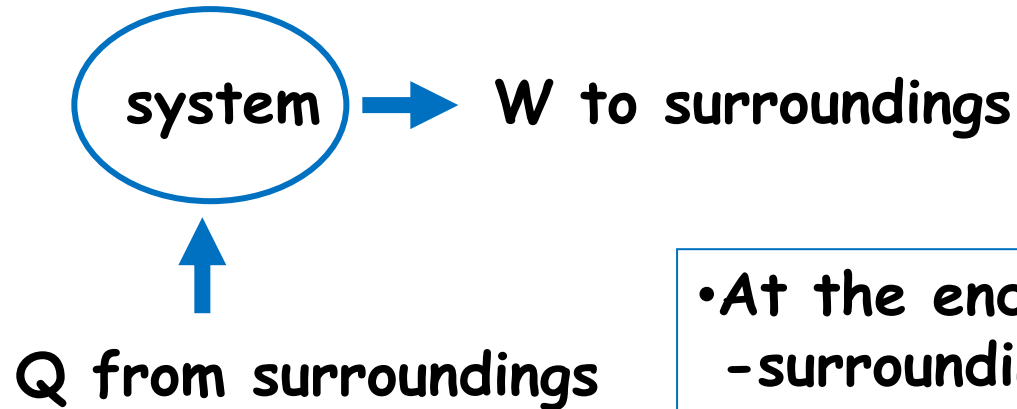
4.1. Reversible, Irreversible Processes and Entropy

a. Reversible processes:

A reversible process is a process that, after it has taken place, can be reversed and causes **no change** in either the system or its surroundings (i.e. without loss or dissipation of energy)



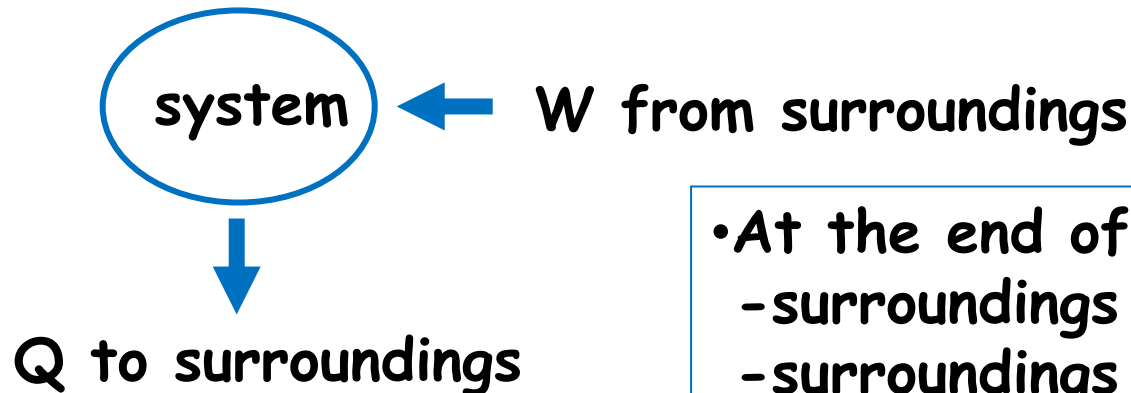
isothermal expansion



$$Q = W = nRT \ln \frac{V_f}{V_i}$$

- At the end of the isothermal expansion:
 - surroundings have received work
 - surroundings have given up heat

isothermal compression



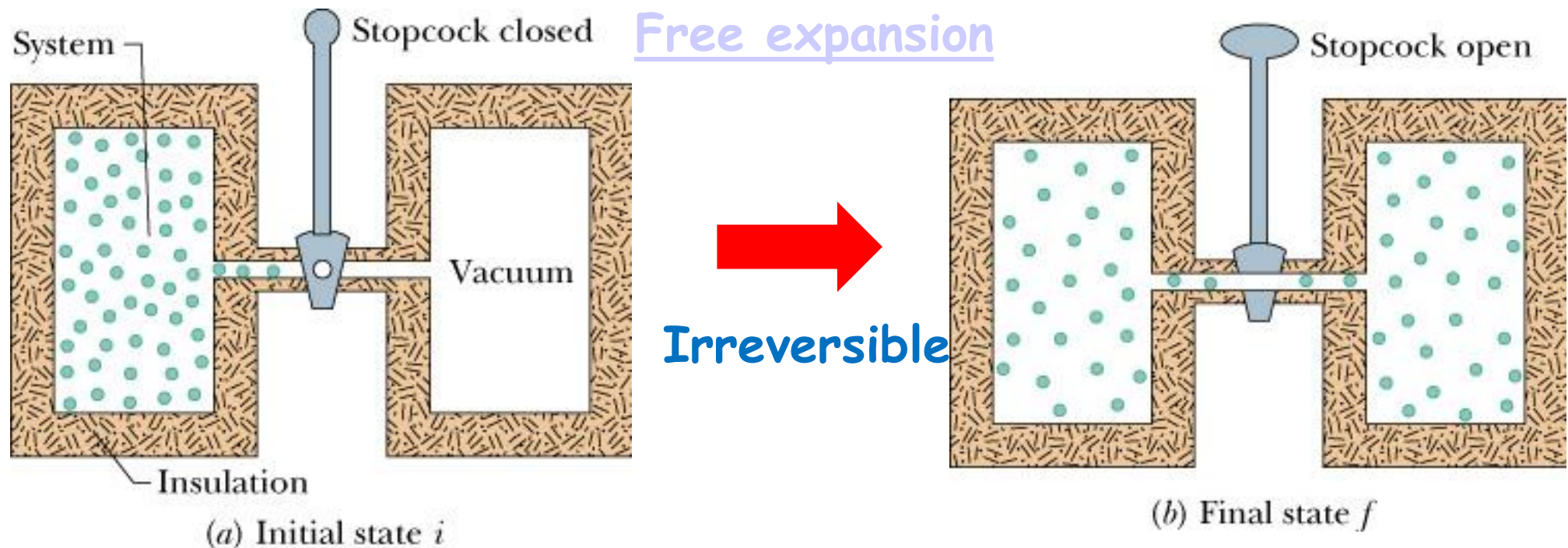
- At the end of the isothermal compression:
 - surroundings have done work
 - surroundings have received heat

Net result: the system and the surroundings back to the initial state without any change \Rightarrow the process is reversible

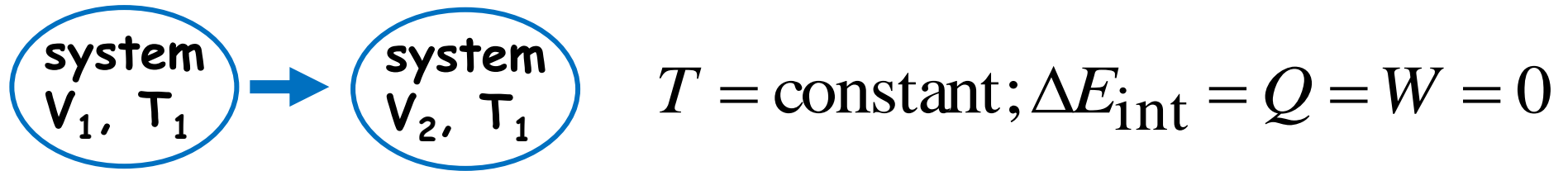
- However, the presence of friction always results in the output work of the system being smaller than the work transferred into the system. Therefore, **it is practically impossible to realize reversible processes** (i.e. ideal ones). But the concept of a reversible process proves to be very useful in studying irreversible processes.

b. Irreversible processes:

- A process that is not reversible is called irreversible.
- In irreversible processes, both the system and the surroundings can not return to their initial state on their own.

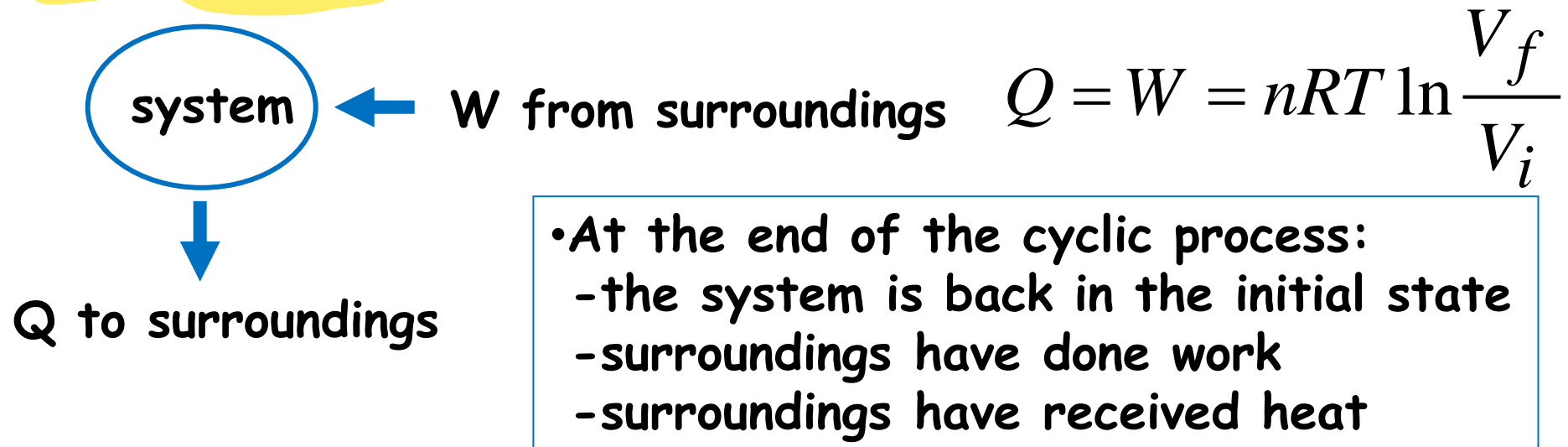


Free expansion



• To restore the system to the initial state at constant T , we compress isothermally by some external agency:

isothermal compression



Net result: the system is the same and the surroundings have changed (W converted to Q)

\Rightarrow the universe has changed \Rightarrow the process is irreversible

•For irreversible processes, the entropy S of a closed system always increases, because of this property, the change in entropy ΔS is sometimes called "the arrow of time".

Examples: eggs \Rightarrow chickens: $\Delta S > 0$
chickens \Rightarrow eggs: $\Delta S < 0$: it never happens

d. Change in Entropy:

There are two equivalent ways to define the change in entropy of a system:

- (1) in terms of the system's temperature and the energy the system gains or loses as heat (next slide)
- (2) by counting the ways in which the atoms or molecules that make up the system can be arranged (see next lecture)

Not in Final

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

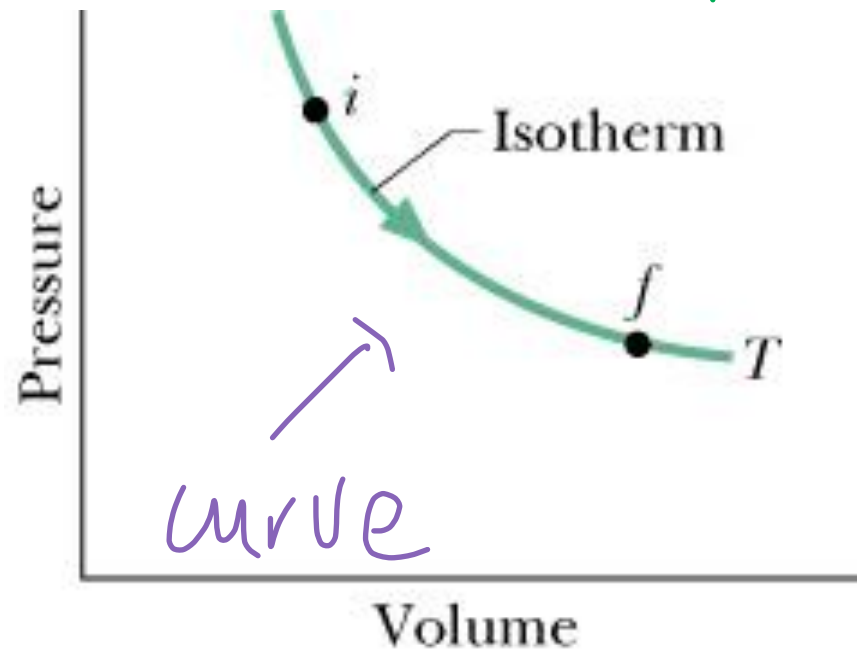
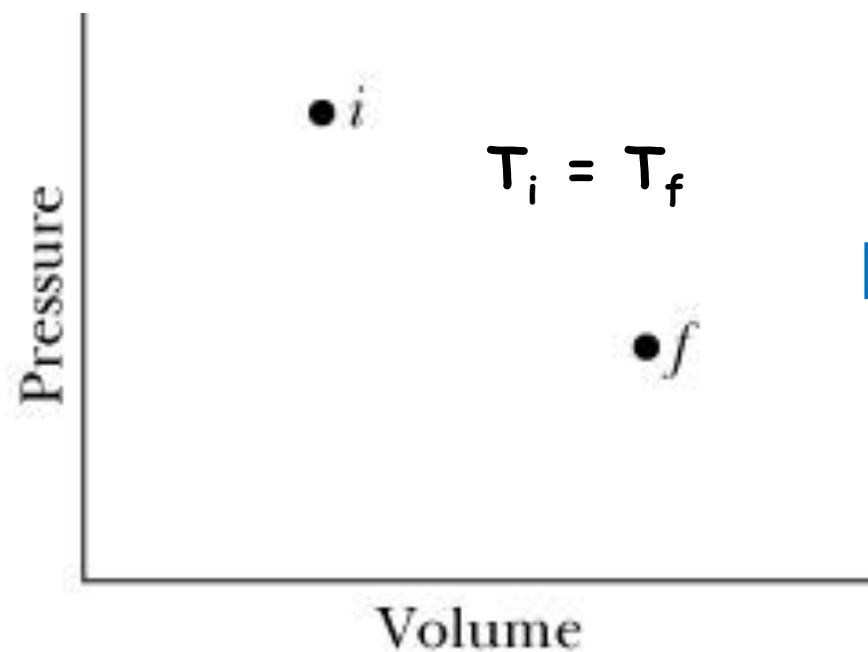
Q: energy transferred as heat to or from the system during the process; **T (K)**: temperature of the system; Unit: **J/K**

- For free expansions: p , V and T fluctuate unpredictably, so we cannot find a relation between Q and T to calculate ΔS .

Method to calculate ΔS :

- The difference in entropy only depends on the initial and final states, we can therefore replace an irreversible process occurring in a closed system with any reversible one that connects the same initial and final states to calculate the entropy change.

- For the case of free expansions:



$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}$$

- For isotherms:

$$Q = W = nRT \ln \frac{V_f}{V_i}$$

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

free expansion:

$$T_i = T_f$$

$$\Delta E_{int} = 0$$

$$Q = 0$$

$$W = 0$$

• **Special Case:** If the temperature change ΔT of a system is small relative to the temperature (in K) before and after the process, the change in entropy can be computed:

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}}$$

Checkpoint 1 (p. 539): Water is heated on a stove. Rank the entropy changes of the water as its temperature rises (a) from 20°C to 30°C , (b) from 30°C to 35°C , and (c) from 80°C to 85°C , greatest first.

5 ✓ $\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}} = \frac{cm\Delta T}{T_{avg}} \Rightarrow (a), (b), (c)$ 5 ✓ 10

Homework: Read Sample Problems page 540 and page 541