

**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  $\Delta E_{\text{int}}$  of the gas, and (d) the change  $\Delta K$  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:  $K_{\text{avg}} = \frac{3}{2}kT \Rightarrow \Delta K_{\text{avg}} = \frac{3}{2}k\Delta T$

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

of Sample

$$C_p = C_v + R$$

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

$3 \times N_A \times \Delta K$

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.

$$1 \text{ atm} = 1.01 \times 10^5 \text{ (Pa)}$$

Equation of state:

$$pV = nRT$$

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

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

For a diatomic gas,  $f=5$ :

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

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

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

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?

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

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

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

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

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?

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

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

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

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

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

(c)

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

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

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

*free expansion*

$$p_0 V_0 T_0 \xrightarrow{\text{free expansion}} p_1 V_1 T_1 \xrightarrow{\quad} p_2 V_2 T_2$$
$$p_0 V_0 = p_1 V_1 \quad p_1 V_1^\gamma = p_2 V_2^\gamma$$
$$T_0 = T_1 \quad p_2 = 3^{1/3} p_0$$
$$V_1 = 3 V_0$$

# 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

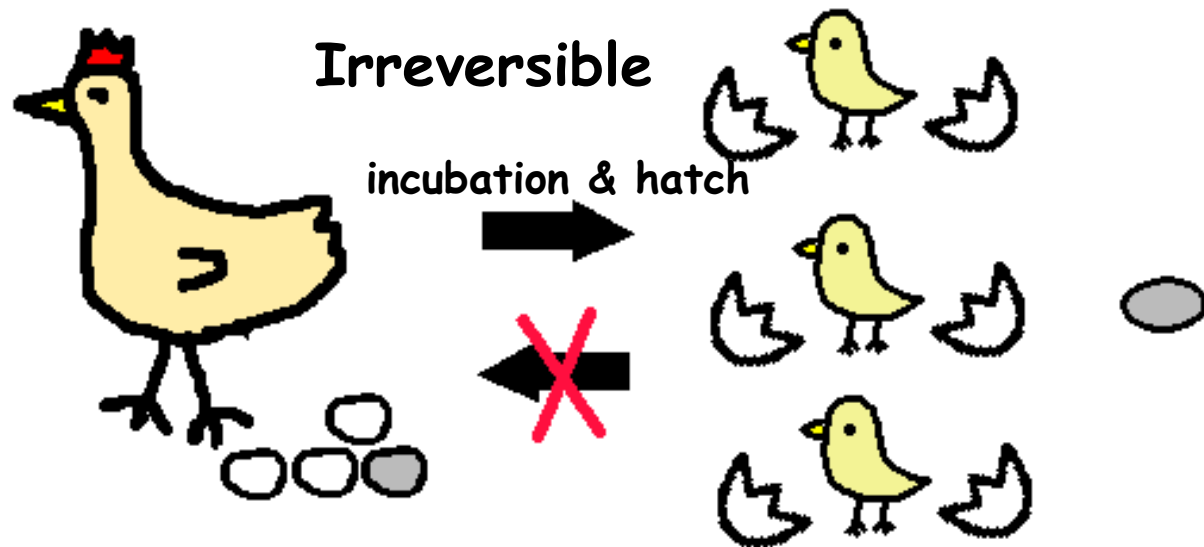
## 4.4. A Statistical View of Entropy



# What is Physics?

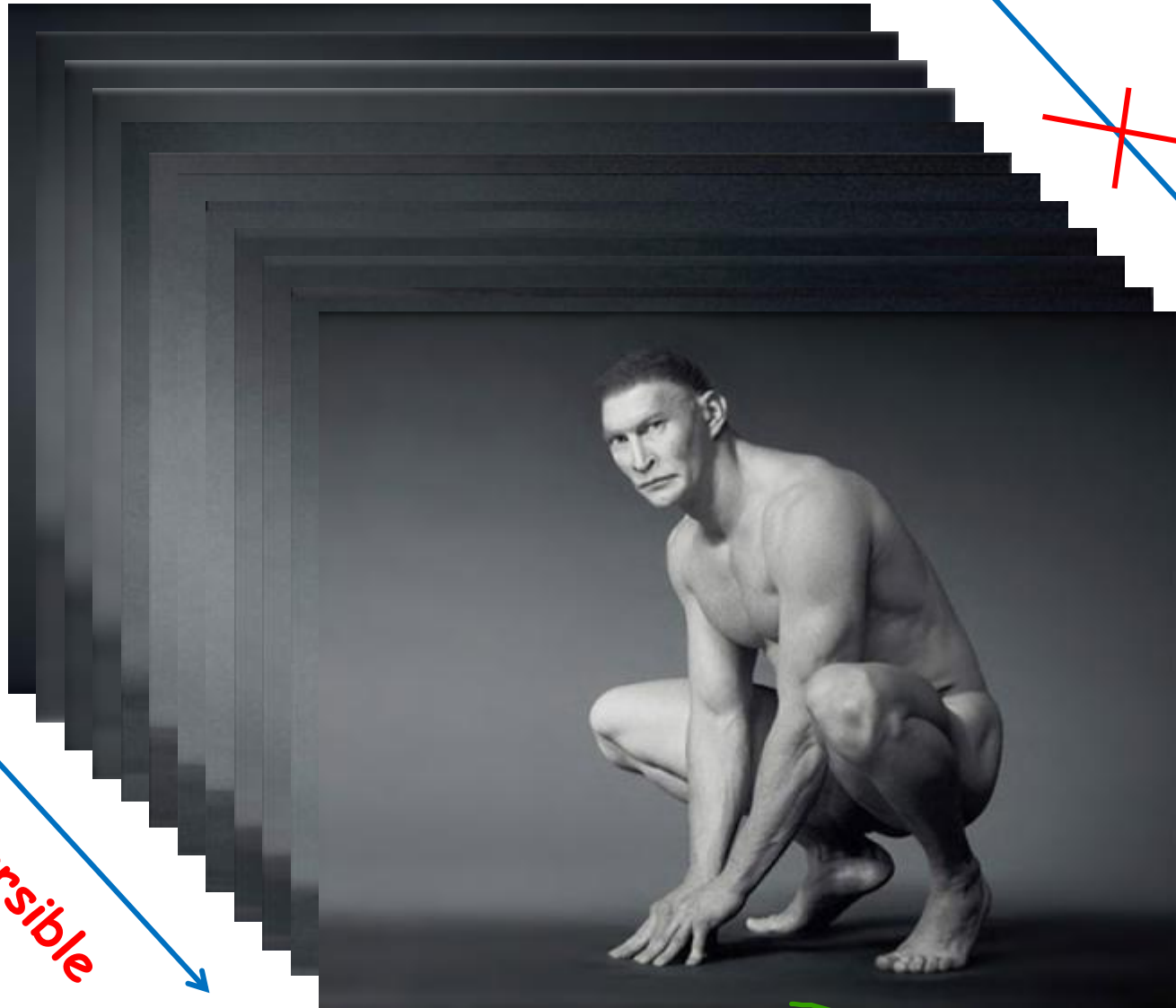
- Time has direction, from the past to the future
- One-way processes that can occur only in a certain sequence and never in the reverse sequence are **irreversible**, meaning that they can not be reversed.

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



# Evolution

Irreversible

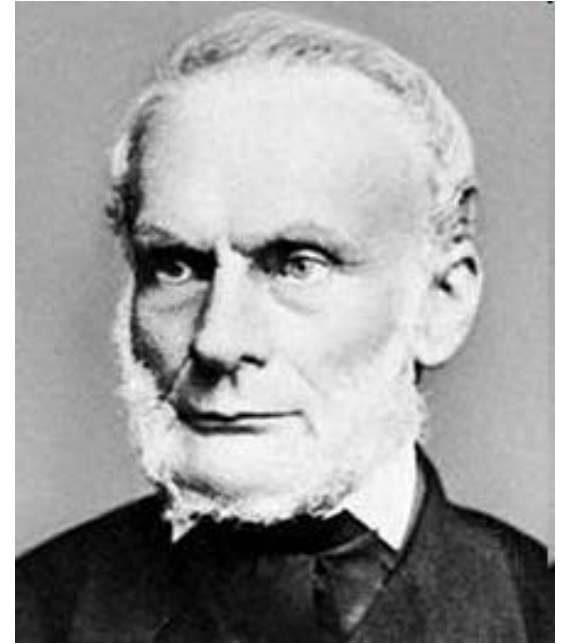


Credit:  
Daniel Lee

- 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

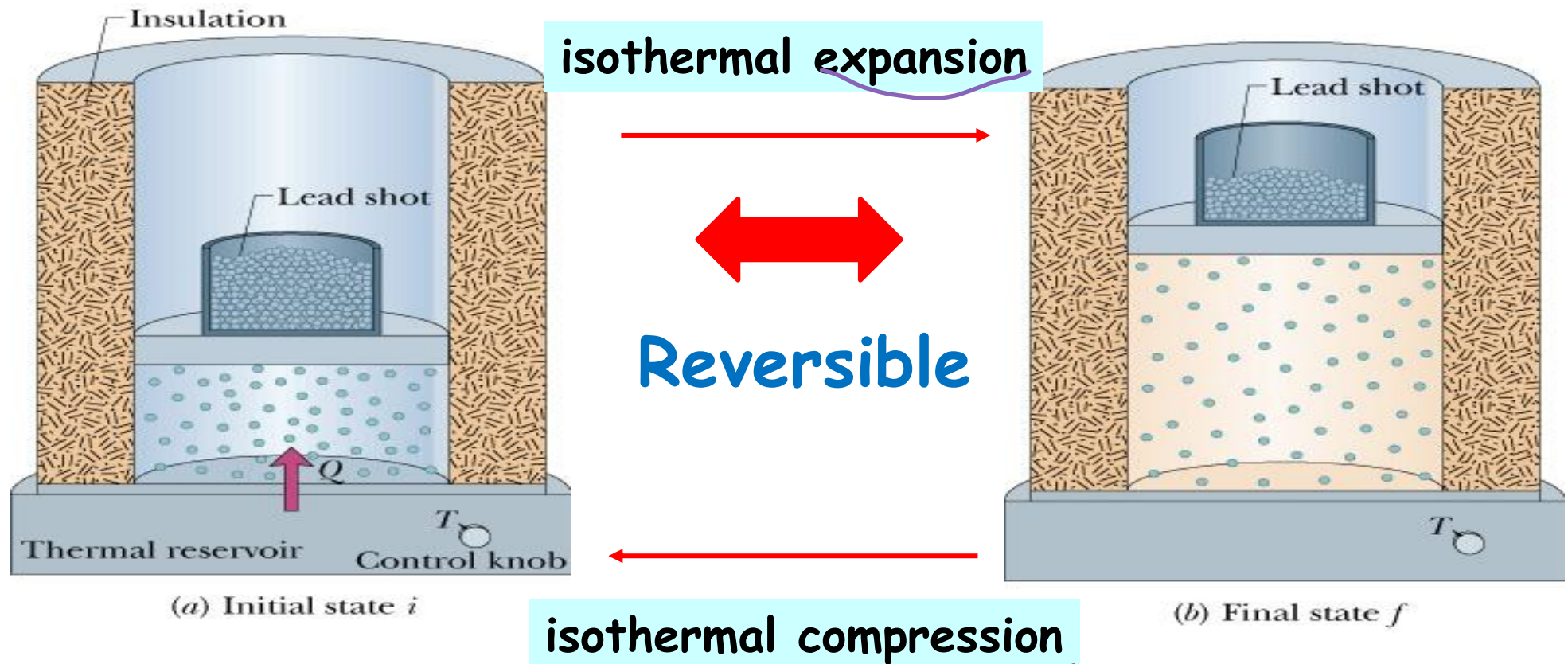
Although the concept of entropy was originally a thermodynamic construct, it has been adapted in the other following fields of study:

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

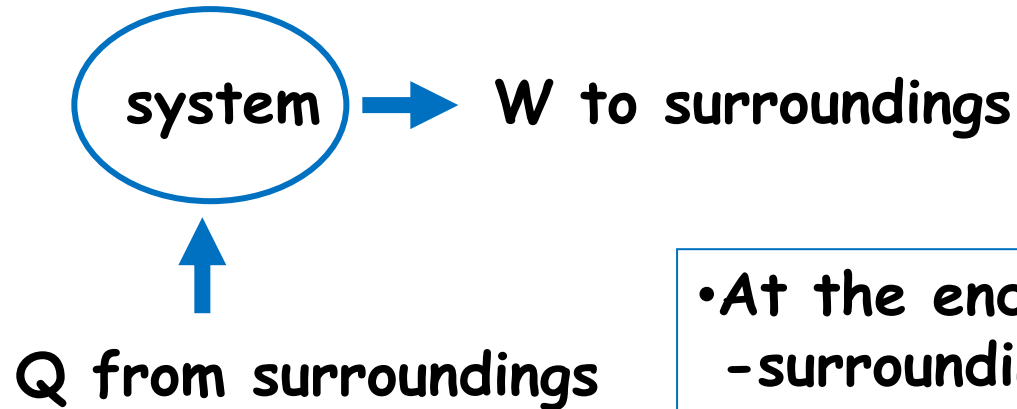
## 4.1. Reversible, Irreversible Processes and Entropy

### 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)



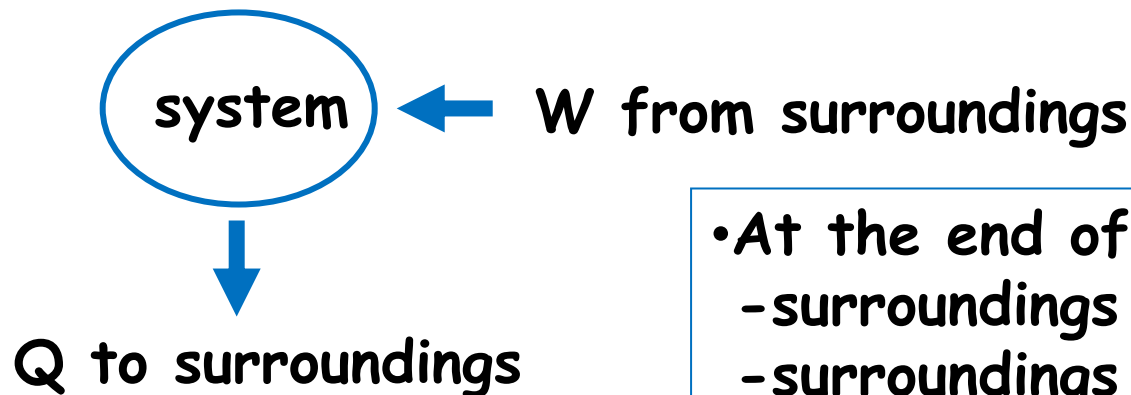
## isothermal expansion



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

- 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

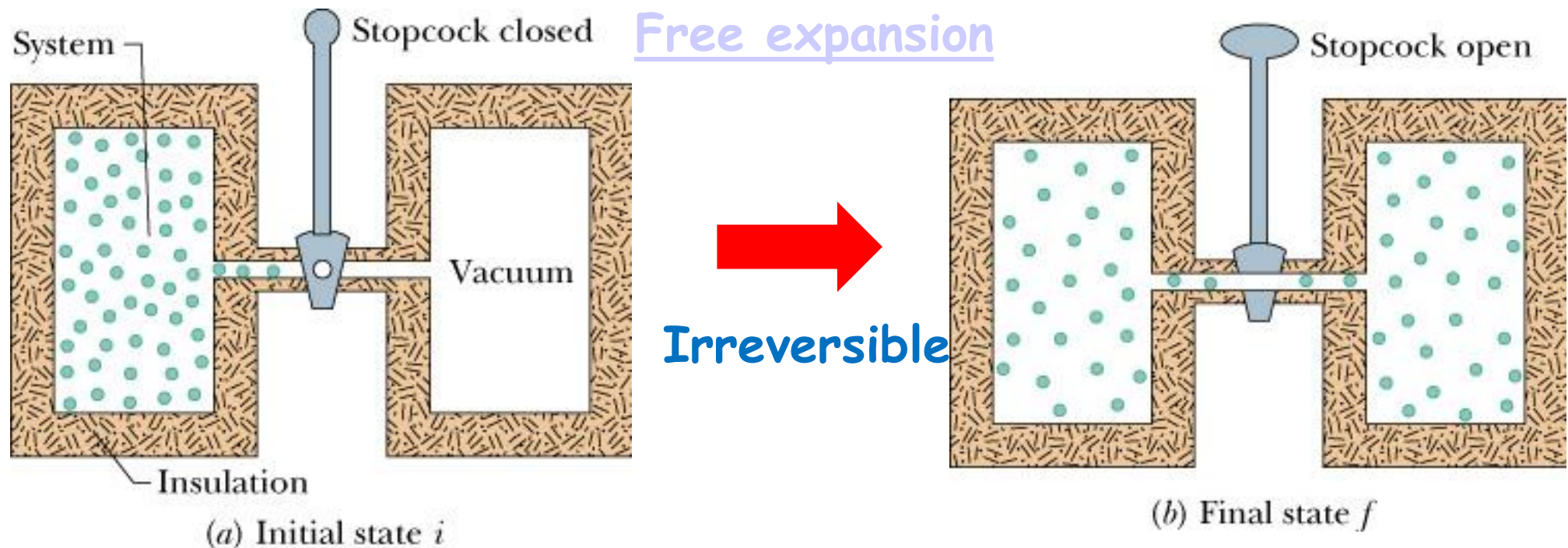
Net result: the system and the surroundings back to the initial state without any change  $\Rightarrow$  the process is reversible



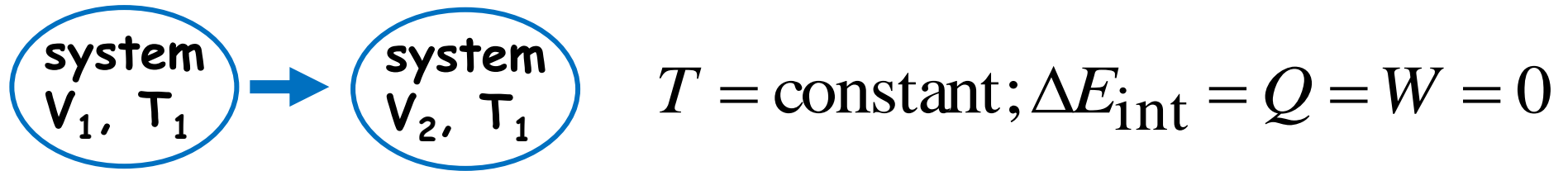
- However, the presence of friction always results in the output work of the system being smaller than the work transferred into the system. Therefore, **it is practically impossible to realize reversible processes** (i.e. ideal ones). But the concept of a reversible process proves to be very useful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

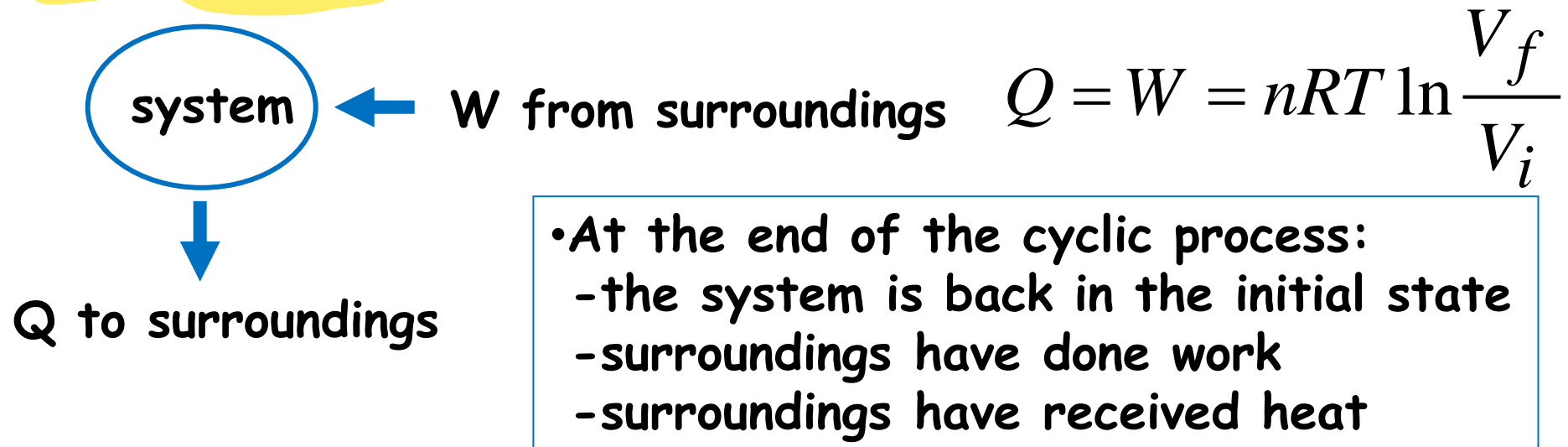


## Free expansion



•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  $\Delta S$  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



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

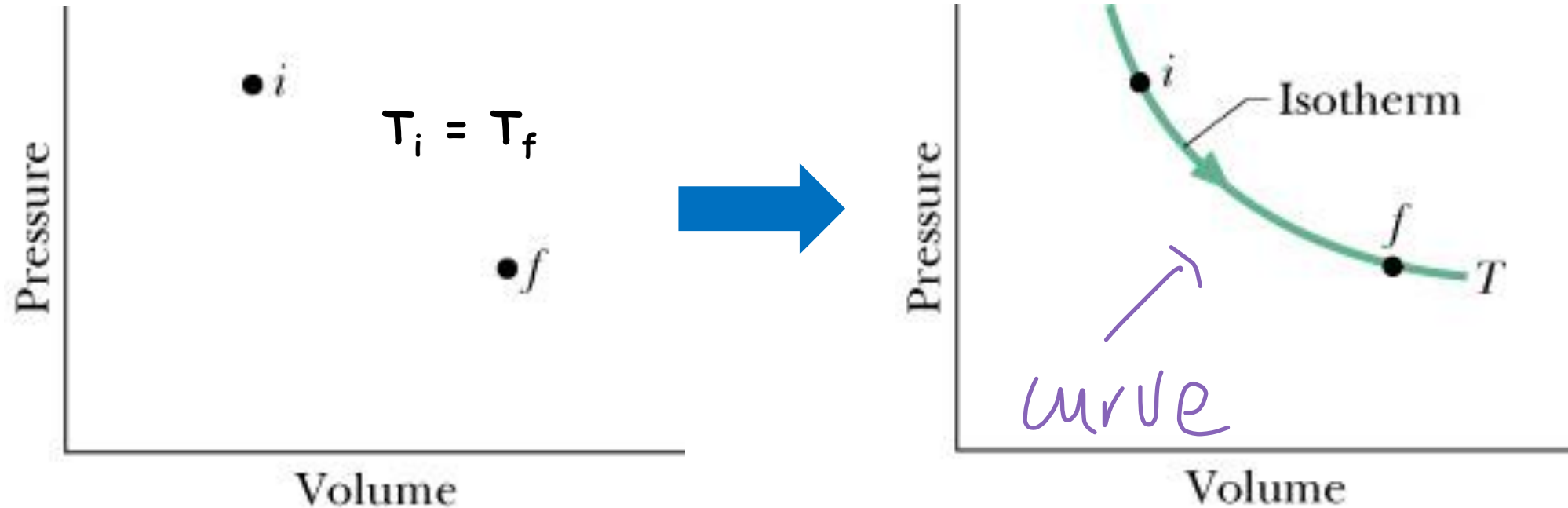
**Q**: energy transferred as heat to or from the system during the process; **T (K)**: temperature of the system; Unit: **J/K**

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

#### **Method to calculate $\Delta S$ :**

- 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:

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

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

• **Special Case:** If the temperature change  $\Delta T$  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  $20^\circ\text{C}$  to  $30^\circ\text{C}$ , (b) from  $30^\circ\text{C}$  to  $35^\circ\text{C}$ , and (c) from  $80^\circ\text{C}$  to  $85^\circ\text{C}$ , 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