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?

$$E = nC_V T$$

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

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

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

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:

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

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

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

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

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:
$$pV = nRT$$

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

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

For a diatomic gas, f=5:
$$\gamma = \frac{7}{5}$$

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

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

56. Suppose 1.0L of a gas with γ=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?

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

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

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

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

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) $\quad p_0 V_0 = p_1 V_1; V_1 = 3V_0 \Rightarrow p_1 = \dfrac{1}{3} p_0$

(b) $\qquad\qquad p_1 V_1^{\gamma} = p'_1 V_0^{\gamma}$

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

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

$f = 6$: polyatomic

(c)

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

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

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

# Chapter 4 Entropy and the Second Law of Thermodynamics
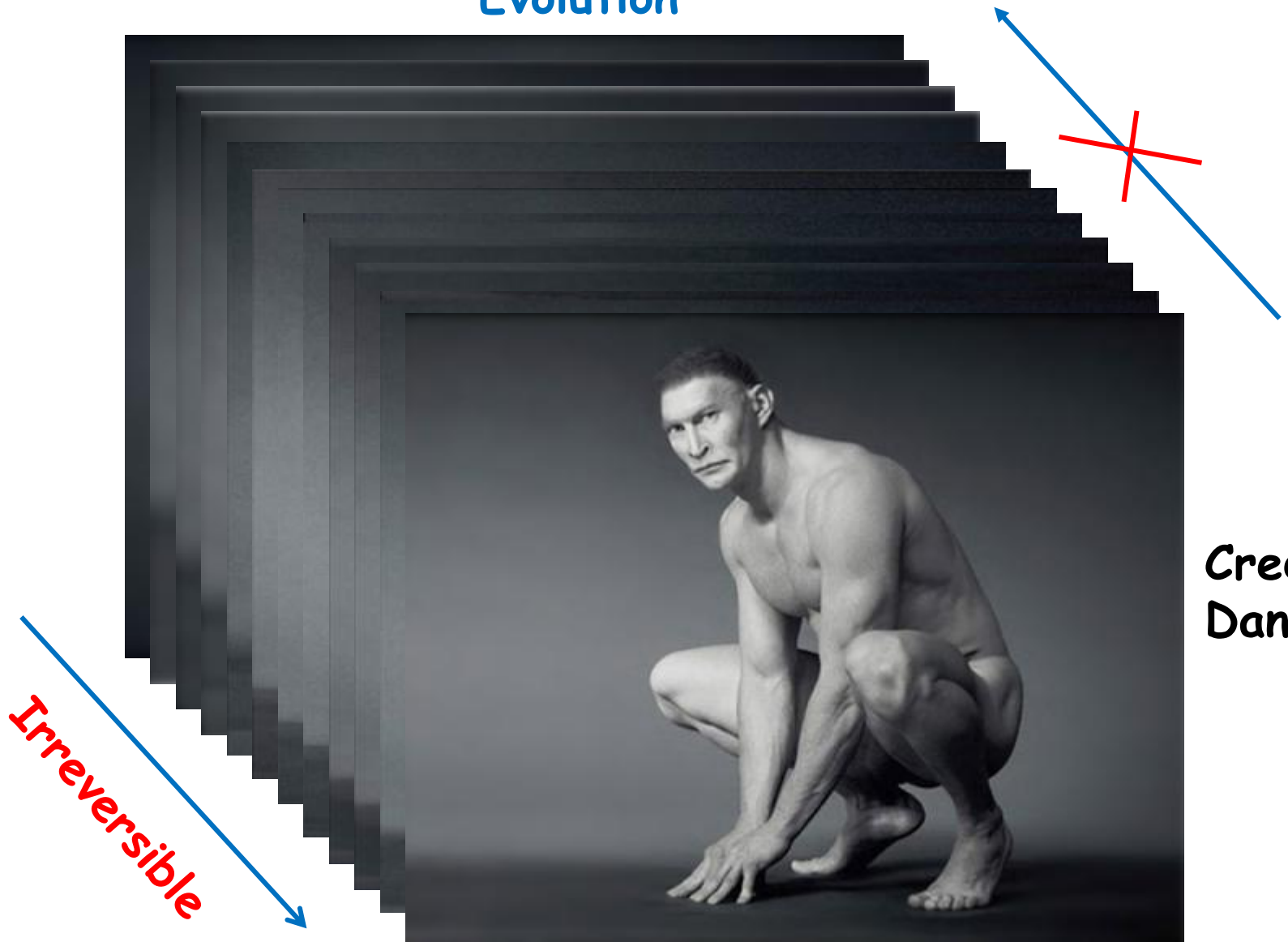
4.1. Reversible, Irreversible Processes and Entropy

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.

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

Irreversible

incubation & hatch
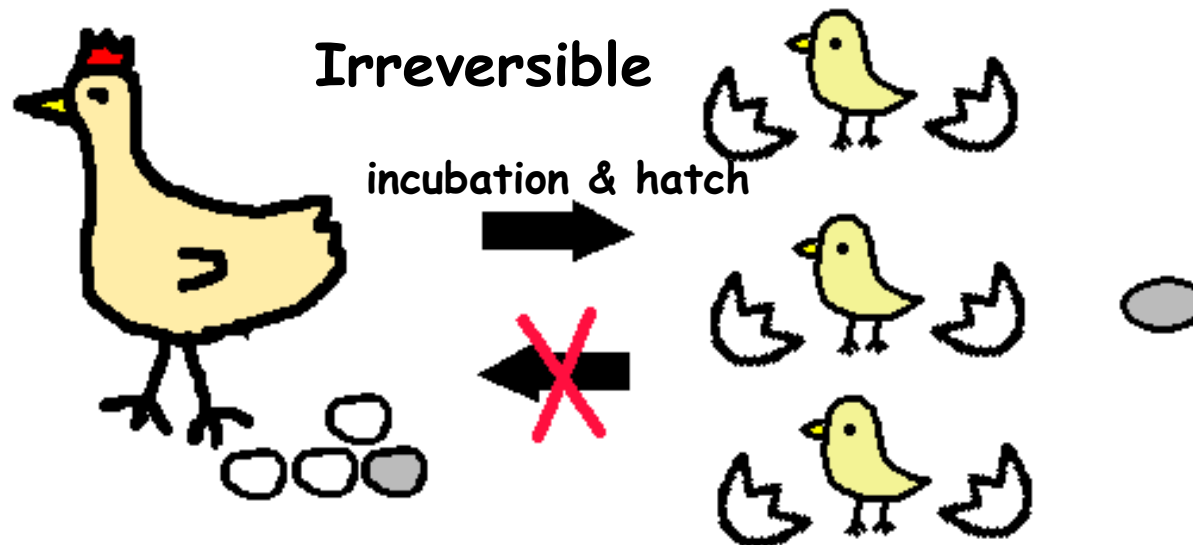
Evolution

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'.
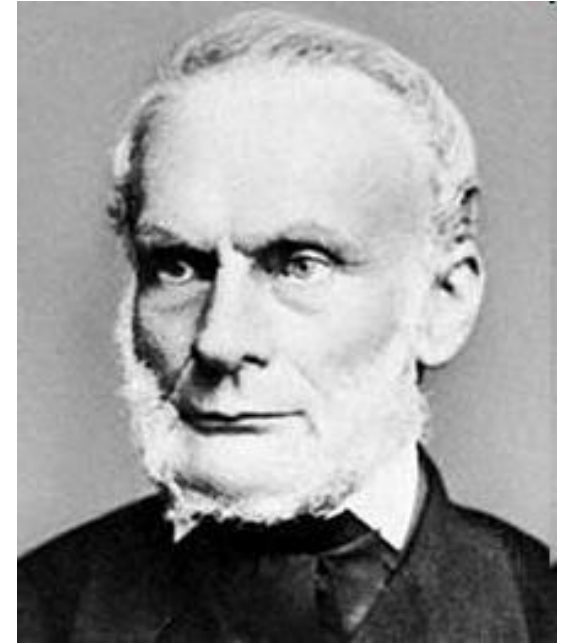
Clausius - author
of the entropy concept

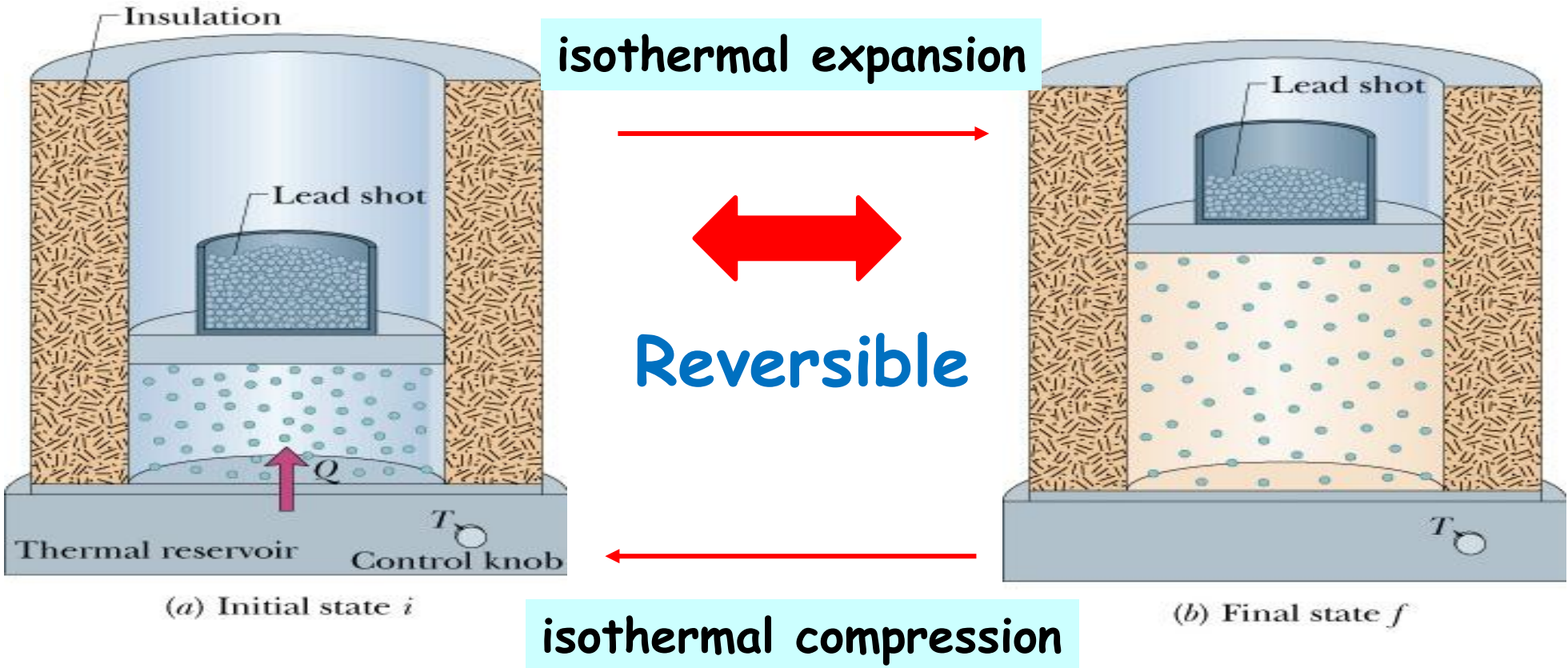## Interdisciplinary applications of entropy

Although the concept of entropy was originally a thermodynamic
construct, it has been adapted in the other following fields of study:
- ✓ information theory
- ✓ psychodynamics
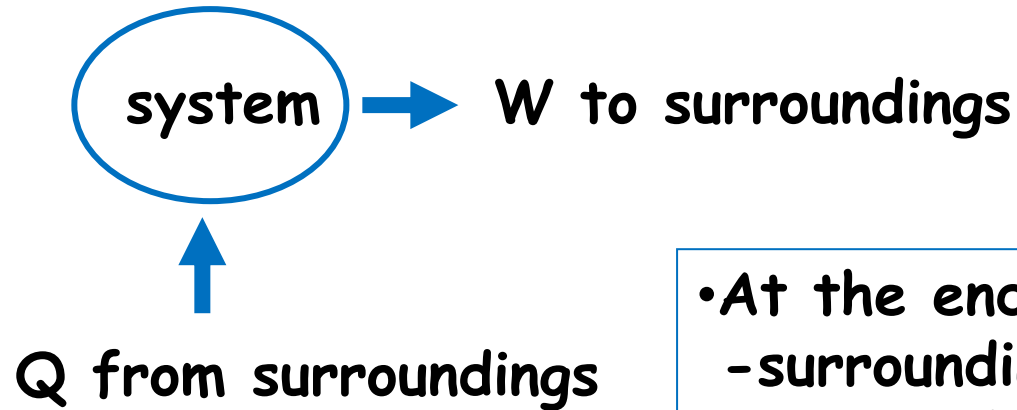- ✓ thermoeconomics
- ✓ evolution

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)
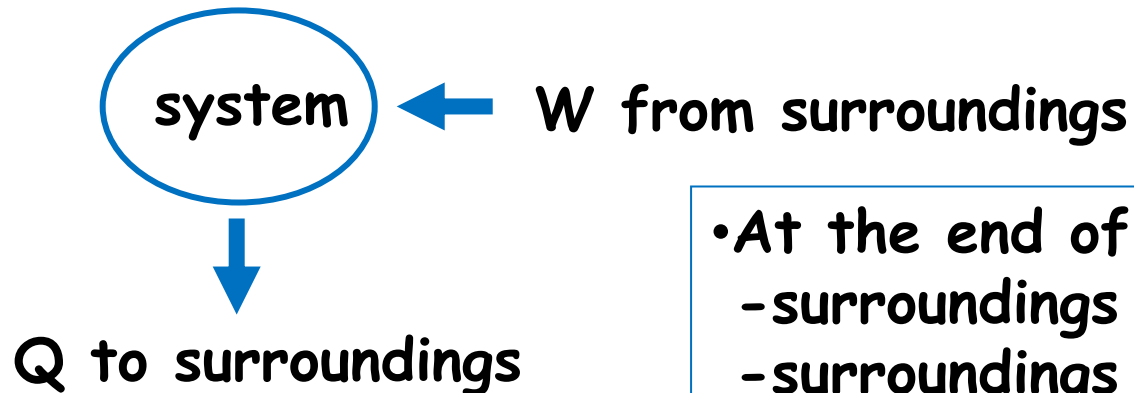

isothermal expansion

Reversible

isothermal compression

(a) Initial state i

(b) Final state f

system → W to surroundings

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

Q from surroundings

•At the end of the isothermal expansion:
  -surroundings have received work
  -surroundings have given up heat
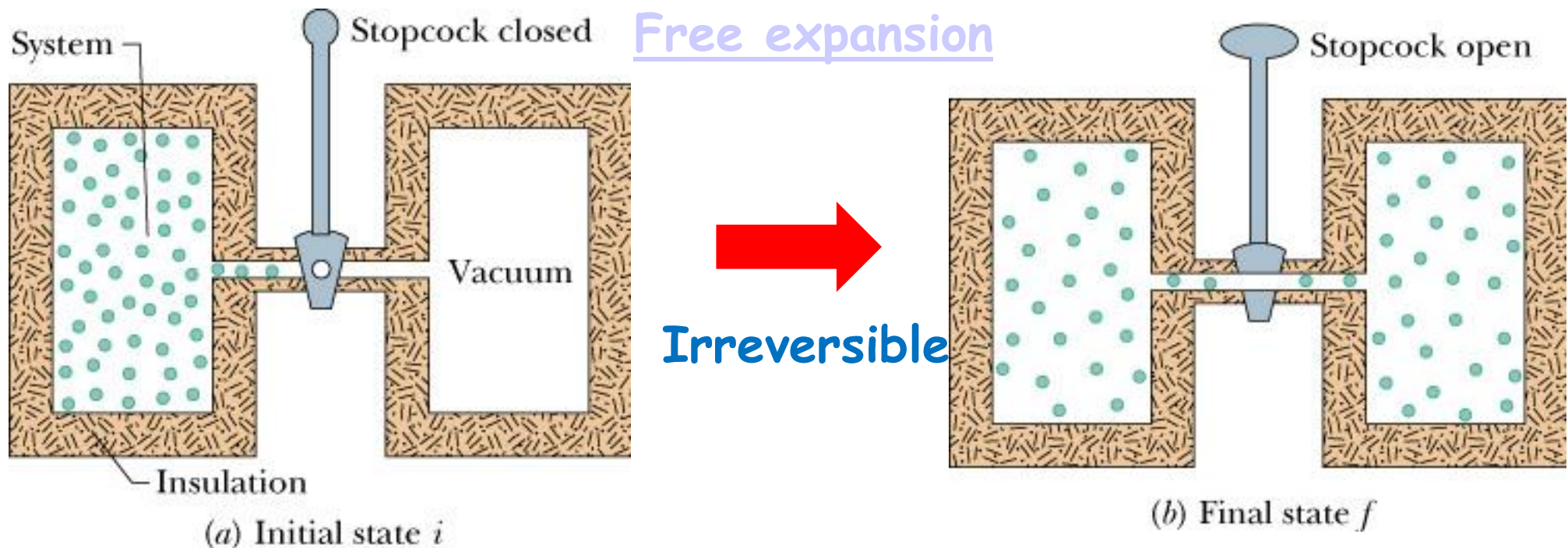
system ← W from surroundings

Q to surroundings

•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 ⇒ 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.
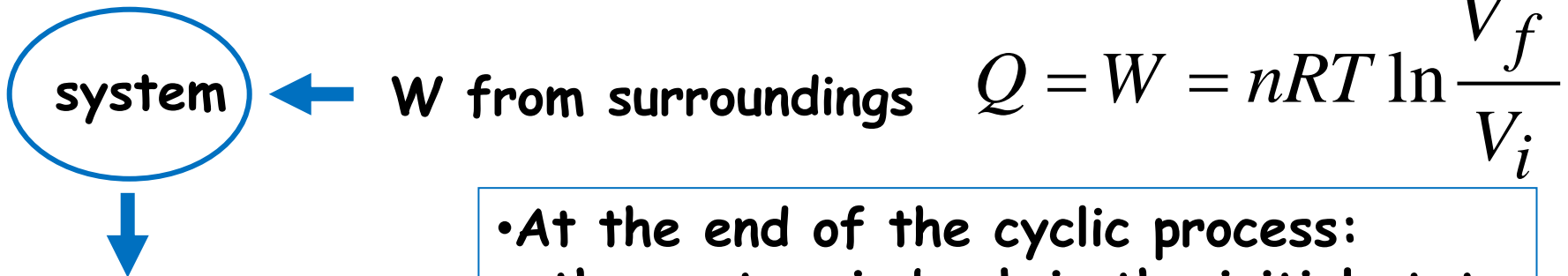

(a) Initial state *i*

(b) Final state *f*

system V_1, T_1 → system V_2, T_1
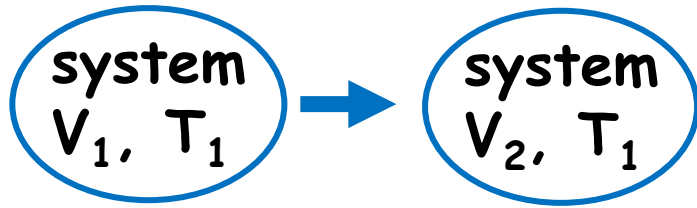
$$T = \text{constant}; \Delta E_{\text{int}} = Q = W = 0$$

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

isothermal compression

system ← W from surroundings

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

↓ Q to surroundings

•At the end of the cyclic process:
 -the system is back in the initial state
 -surroundings have done work
 -surroundings have received heat

<u>Net result</u>: the system is the same and the surroundings have changed (W converted to Q)
⇒ the universe has changed ⇒ **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)

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

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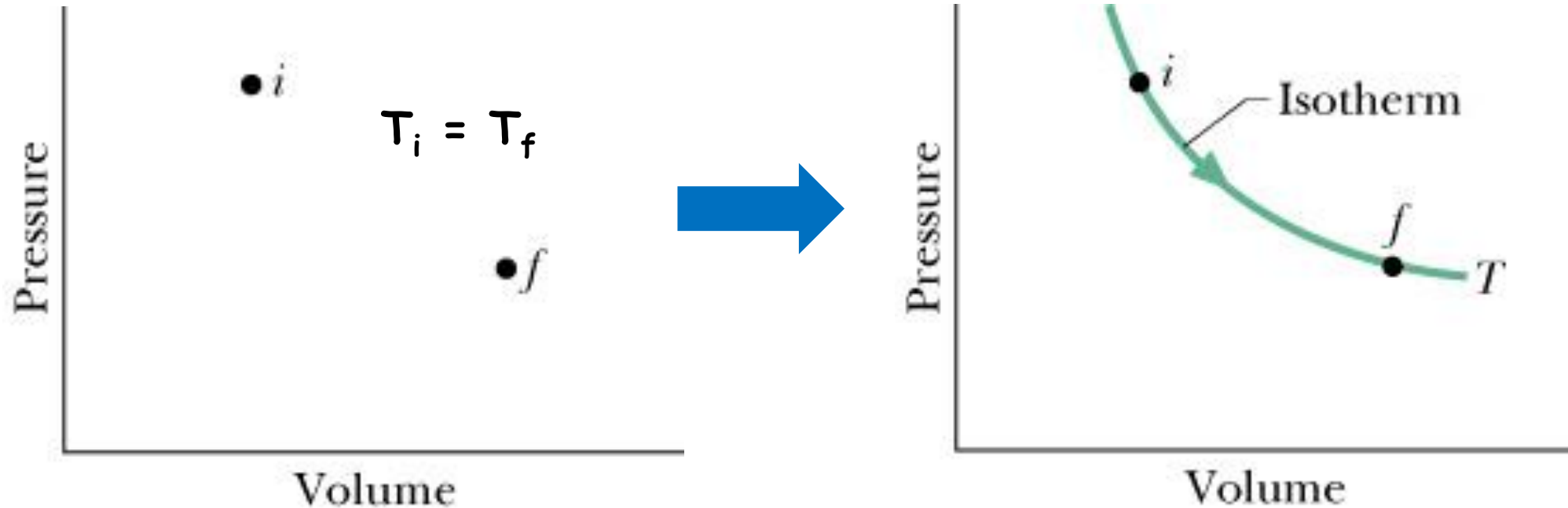
$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}$$

- **For isotherms:**

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

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

• **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 20⁰C to 30⁰C, (b) from 30⁰C to 35⁰C, and (c) from 80⁰C to 85⁰C, greatest first.

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

Homework: Read Sample Problems page 540 and page 541