

Gaussian integrals

$$\langle U^2 \rangle = 3 \langle U_x^2 \rangle \quad f(U_x) = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT} U_x^2}$$

.3/2 m

$$\langle U_x^2 \rangle = \int dU_x U_x^2 f(U_x)$$

$$\int_{-\infty}^{\infty} dx e^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}} = I(\lambda)$$

$$\int_{-\infty}^{\infty} dx x^2 e^{-\lambda x^2} = \frac{1}{2} \sqrt{\frac{\pi}{\lambda^3}}$$

$$\frac{d}{d\lambda} I(\lambda) = \int_{-\infty}^{\infty} dx x^2 e^{-\lambda x^2}$$

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}),$$

$$v_p = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}),$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (\text{rms speed}).$$

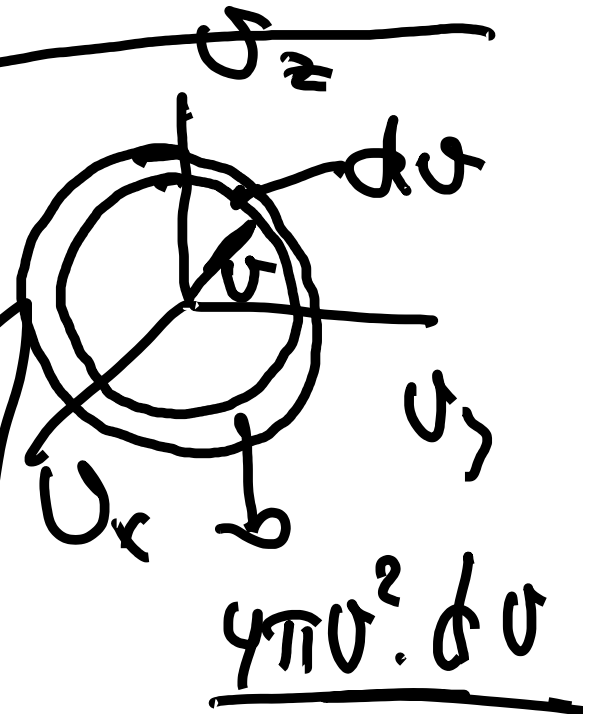
$$f(u_x) = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT} u_x^2}$$

$$\int_{-\infty}^{\infty} du_x f(u_x) = 1$$

$$\underline{F(u_x, u_y, u_z)} = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} u^2}$$

$$P(u) du = \int F(u_x, u_y, u_z) =$$

$$P(u) = 4\pi u^2 \cdot \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} u^2}$$



Kinetic Theory of Gases

- relates the macroscopic properties of gases to the microscopic properties of gas molecules.

Avogadro's Number

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad \text{Eq. 19-1}$$

- Mole related to mass of a molecule

$$M = mN_A \quad \text{Eq. 19-4}$$

Ideal Gas

An ideal gas is one for which the pressure p , volume V , and temperature T are related by

$$pV = nRT \quad (\text{ideal gas law}). \quad \text{Eq. 19-5}$$

Temperature and Kinetic Energy

- The average translational kinetic energy per molecule of an ideal gas is

$$K_{\text{avg}} = \frac{3}{2}kT. \quad \text{Eq. 19-24}$$

Maxwell Speed Distribution

- The three measures of distribution of speed

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}),$$

Eq. 19-31

$$v_P = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}),$$

Eq. 19-35

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (\text{rms speed}).$$

Eq. 19-22

Entropy and the Second Law of Thermodynamics

Learning Objectives

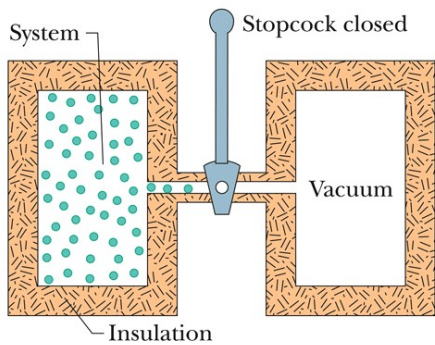
- **20.01** Identify the second law of thermodynamics: If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes; it never decreases.
- **20.02** Identify that entropy is a state function (the value for a particular state of the system does not depend on how that state is reached).
- **20.03** Calculate the change in entropy for a process by integrating the inverse of the temperature (in kelvins) with respect to the heat Q transferred during the process.
- **20.04** For a phase change with a constant temperature process, apply the relationship between the entropy change ΔS , the total transferred heat Q , and the temperature T (in kelvins).

Learning Objectives (Continued)

- **20.05** For a temperature change ΔT that is small relative to the temperature T , apply the relationship between the entropy change ΔS , the transferred heat Q , and the average temperature T_{avg} (in kelvins).
- **20.06** For an ideal gas, apply the relationship between the entropy change ΔS and the initial and final values of the pressure and volume.
- **20.07** Identify that if a process is an irreversible one, the integration for the entropy change must be done for a reversible process that takes the system between the same initial and final states as the irreversible process.
- **20.08** For stretched rubber, relate the elastic force to the rate at which the rubber's entropy changes with the change in the stretching distance.

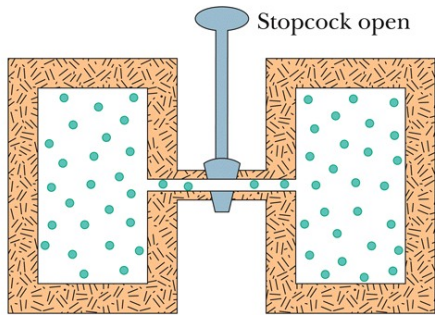


If an irreversible process occurs in a *closed* system, the entropy S of the system always increases; it never decreases.



(a) Initial state i

Irreversible process

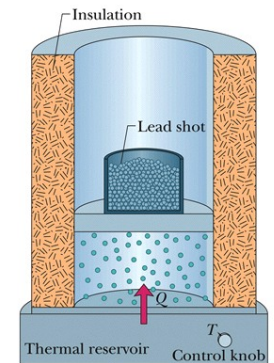


(b) Final state f

This process is irreversible; that is, it does not occur in reverse, with the gas spontaneously collecting itself in the left half of the container.

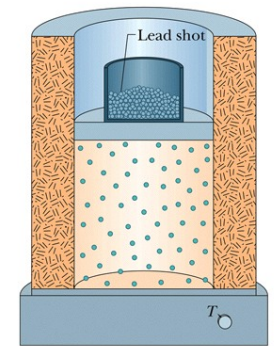
The isothermal expansion of an ideal gas, done in a reversible way.

If a process occurs in a closed system, the entropy of the system **increases** for **irreversible** processes and remains **constant** for **reversible** processes.



(a) Initial state i

Reversible process



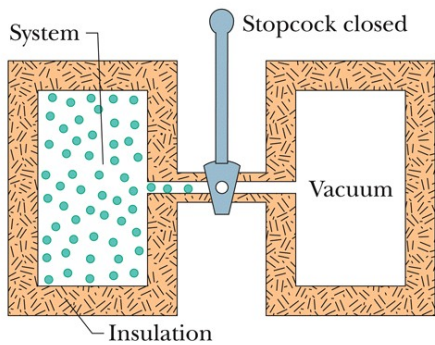
(b) Final state f

Change in Entropy

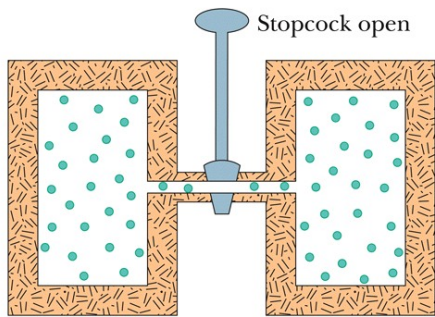
$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

Here Q is the energy transferred as heat to or from the system during the process, and T is the temperature of the system in kelvins during the process.

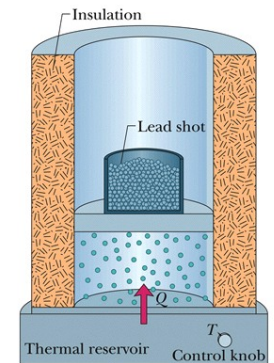
To find the entropy change for an irreversible process, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process with the above equation.



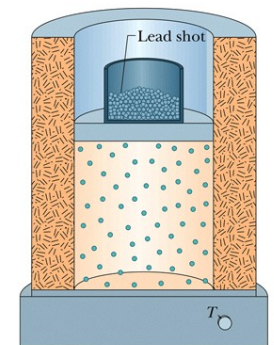
(a) Initial state i



(b) Final state f



(a) Initial state i



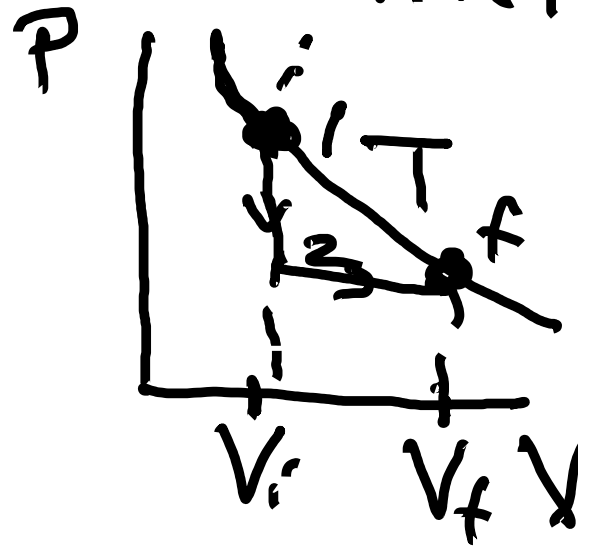
(b) Final state f

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

$$\int dQ$$

$$\Delta E_{int} = Q - W = 0 \Rightarrow$$

$$Q = W$$



$$\int_i^f \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{PdV}{T} = \int_{V_i}^{V_f} \frac{nRT}{TV} dV = nR \ln \frac{V_f}{V_i}$$

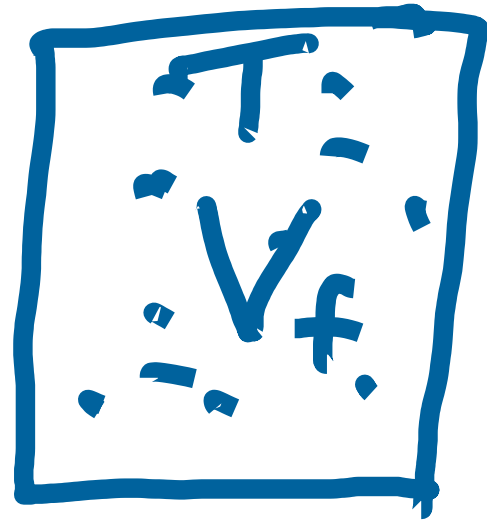
$$\int_i^f dQ \neq \int_i^f dQ = Q_f - Q_i \quad S = nR \ln V + \lambda(T)$$

Free expansion



$$\int \frac{dQ}{T} = 0$$

→



$$\Delta E_{int} = Q - W = 0$$

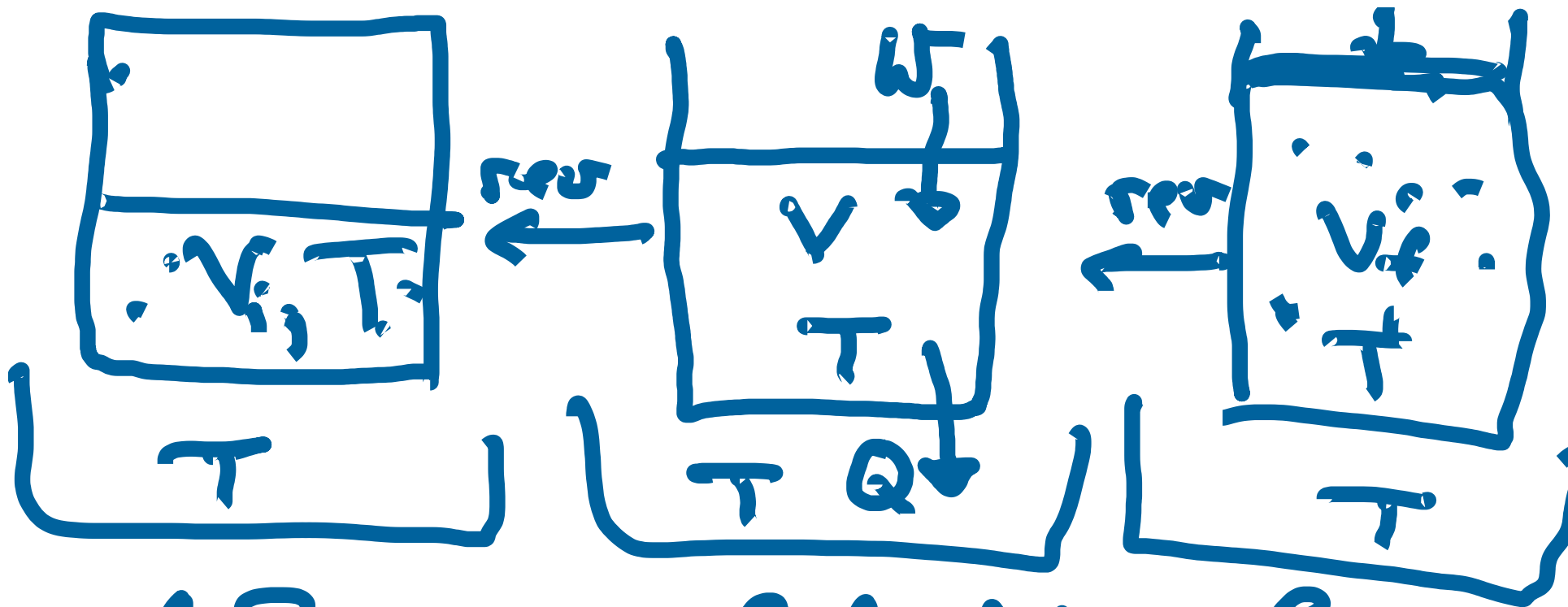
$$\Delta S_{univ} > 0.$$

$$\Delta S_{gas} = nR \ln \frac{V_f}{V_i}$$

$$\Delta S_{gas} + \Delta S_{env} > 0$$

$$\Delta S = \int_{rev} \frac{dQ}{T}$$

$$\Delta S_{env} = 0$$



$$\Delta S_{\text{gas}} = -nR \ln \frac{V_f}{V_i}$$

$$\Delta S_{\text{env}} = +nR \ln \frac{V_f}{V_i}$$



$$\Delta S_{\text{univ}} = 0 \quad \Delta S_{\text{univ}} = nR \ln \frac{V_f}{V_i}$$

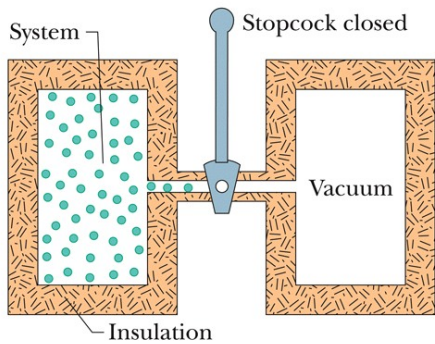


If a process occurs in a *closed* system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

The Second Law of Thermodynamics

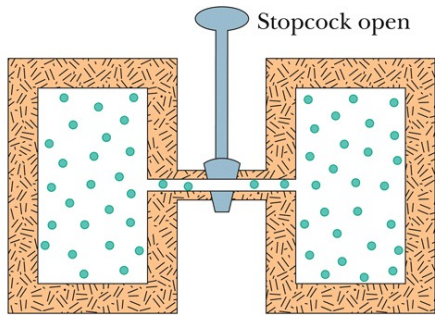
$$\Delta S \geq 0 \quad (\text{second law of thermodynamics}),$$

where the greater-than sign applies to irreversible processes and the equals sign to reversible processes. Equation applies only to closed systems.

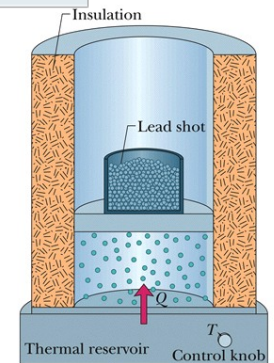


(a) Initial state *i*

Irreversible process

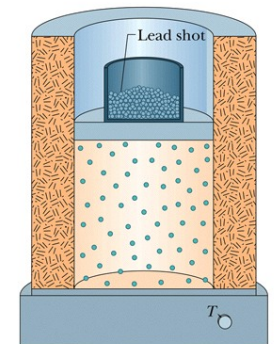


(b) Final state *f*

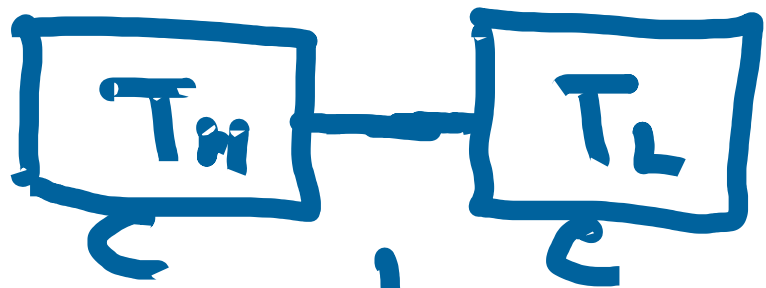


(a) Initial state *i*

Reversible process

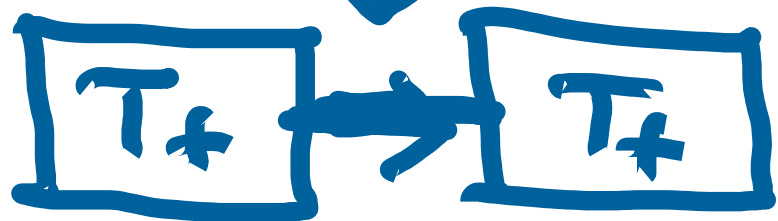


(b) Final state *f*



$$T_H > T_L$$

$$dQ = C dT$$



$$\Delta S_H = \int_{T_H}^{T_f} \frac{dQ}{T} = C \int_{T_H}^{T_f} \frac{dT}{T} = C \ln \frac{T_f}{T_H}$$

$$\Delta S_L = C \ln \frac{T_f}{T_L} = C$$

$$\Delta S = \Delta S_H + \Delta S_L = C \ln \frac{T_f^2}{T_L T_H} > 0$$

$$\Delta S = C \ln \left(\frac{T_f^2}{T_H T_L} \right) > 0$$

$$T_f = \frac{T_H + T_L}{2}$$

$$\left(\frac{T_H + T_L}{2} \right)^2 > T_H T_L \Rightarrow$$

$$(T_H + T_L)^2 > 4 T_H T_L \Rightarrow T_H^2 + T_L^2 + 2 T_H T_L > 4 T_H T_L$$

$$T_H^2 + T_L^2 - 2 T_H T_L = (T_H - T_L)^2 > 0$$