Lecture 25: Heat and The 1st Law of Thermodynamics
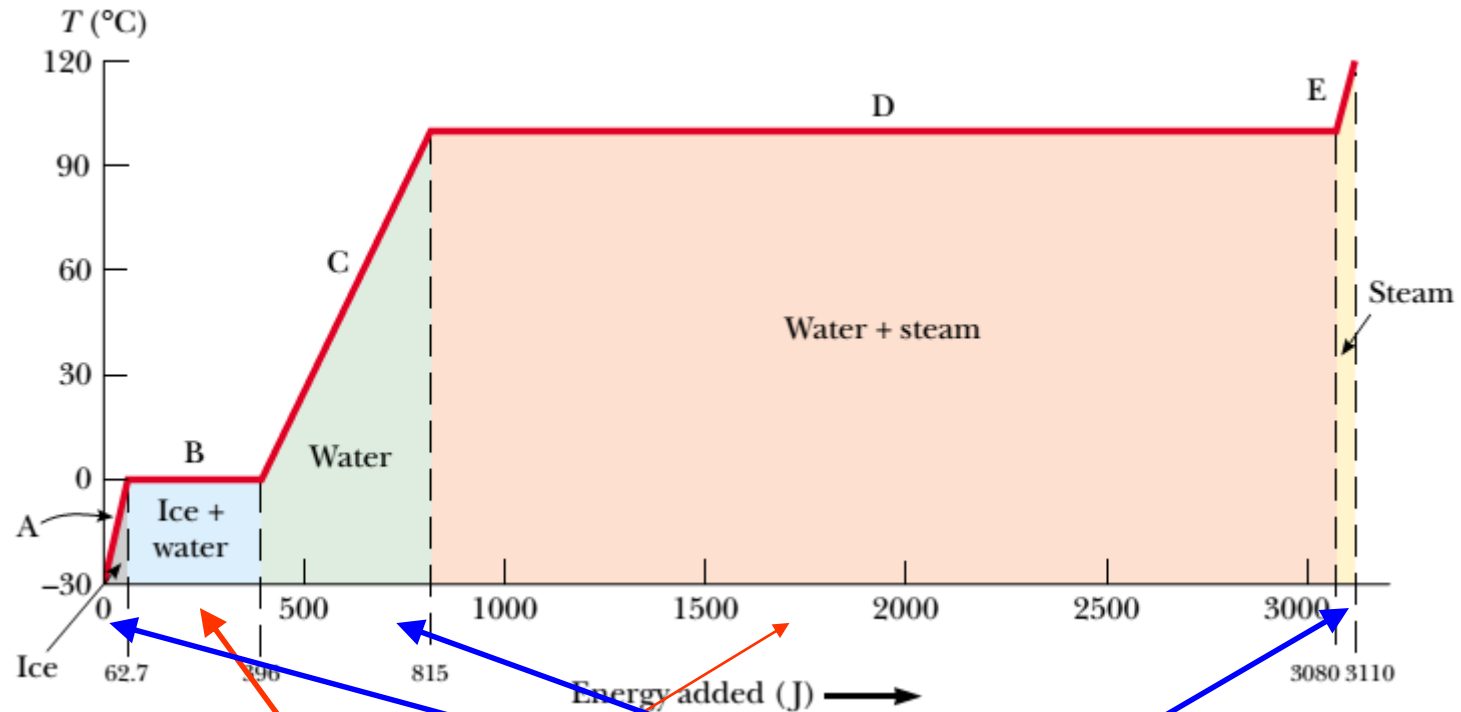
Latent Heat

TABLE 20.2   **Latent Heats of Fusion and Vaporization**

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	-269.65	5.23×10^3	-268.93	2.09×10^4
Nitrogen	-209.97	2.55×10^4	-195.81	2.01×10^5
Oxygen	-218.79	1.38×10^4	-182.97	2.13×10^5
Ethyl alcohol	-114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	$1\,750$	8.70×10^5
Aluminum	660	3.97×10^5	$2\,450$	1.14×10^7
Silver	960.80	8.82×10^4	$2\,193$	2.33×10^6
Gold	$1\,063.00$	6.44×10^4	$2\,660$	1.58×10^6
Copper	$1\,083$	1.34×10^5	$1\,187$	5.06×10^6

The latent heat of vaporization for a given substance is usually somewhat higher than the latent heat of fusion. Why?
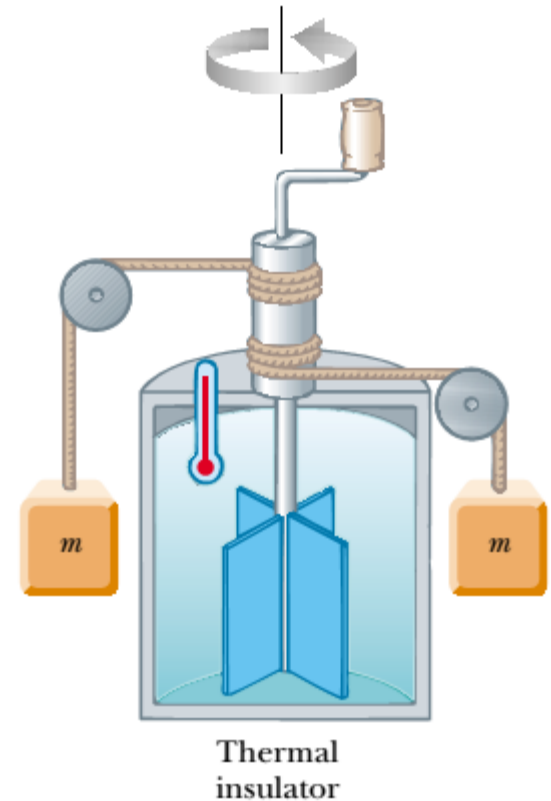
Mechanical Equivalence of Heat

$$1 \text{ cal} \equiv 4.186 \text{ J}$$

The amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.
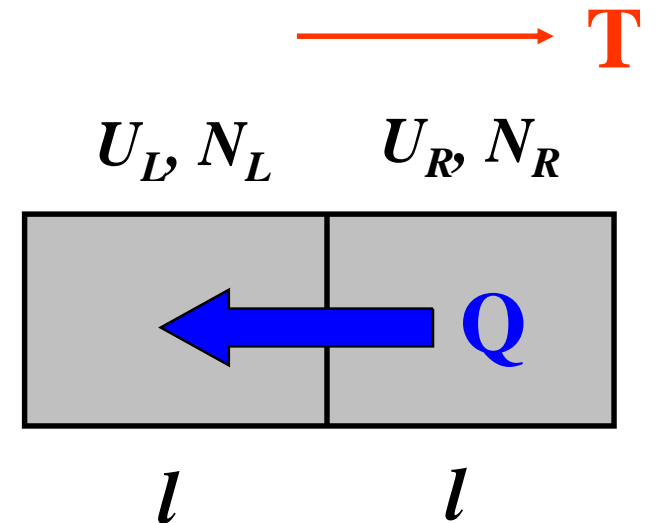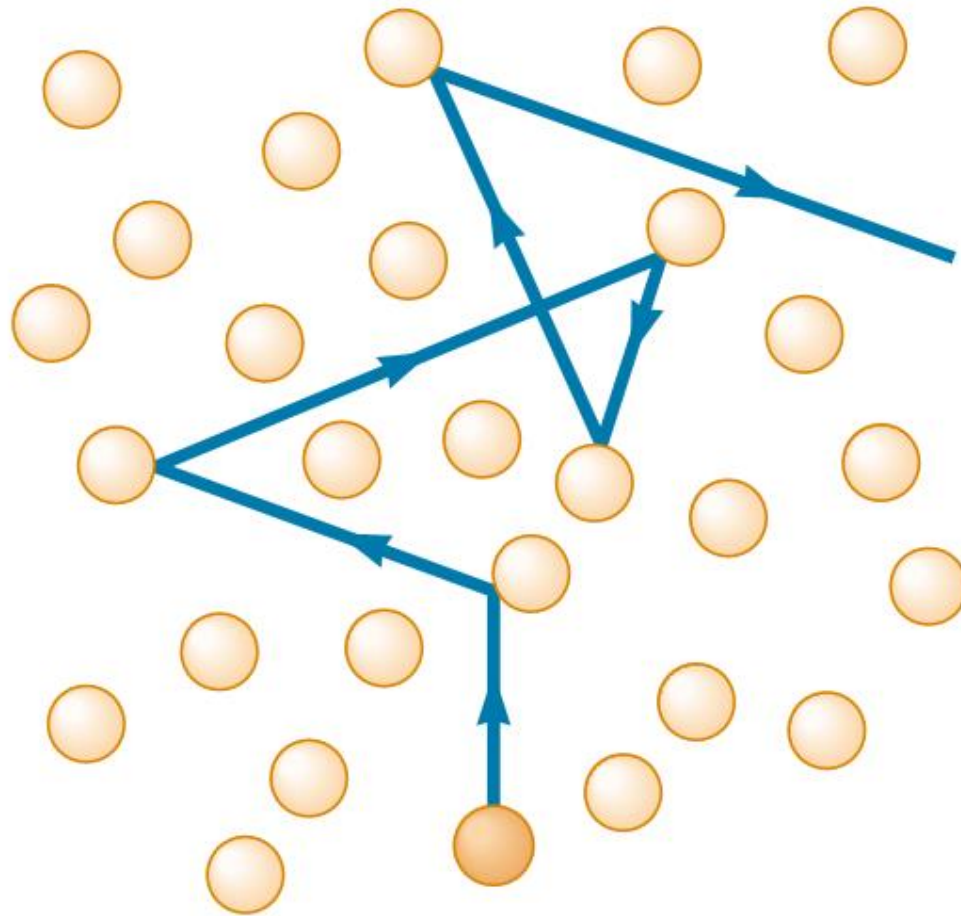
m

m

Thermal insulator

Heat

Heat is defined as the transfer of **energy** across the boundary of a system due to a **temperature** difference between the system and its surroundings.

Heat transfer

– Conduction, convection, radiation

U_L, N_L U_R, N_R

T

Q

l l

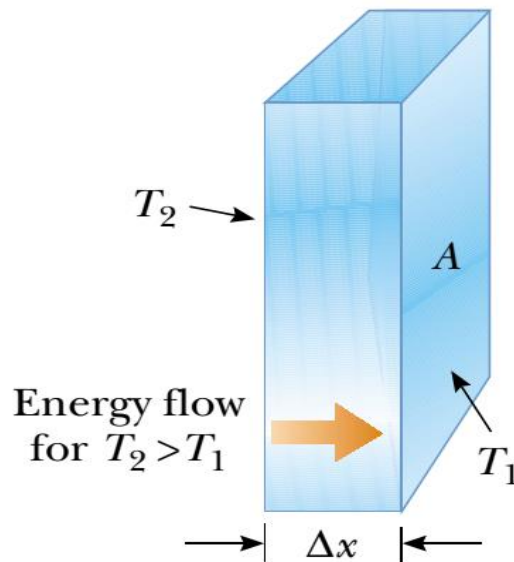# Heat Conduction: Macroscopic
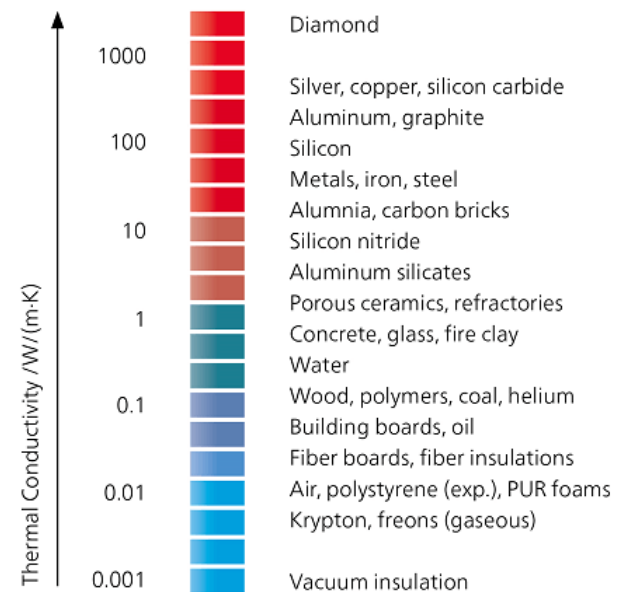
$$\frac{Q}{\Delta t} \propto A \frac{\Delta T}{\Delta x}$$

Fourier heat conduction law

$$\frac{Q}{\Delta t} = -\kappa_t A \frac{dT}{dx}$$

Remind you of Ohm's law?

(Thermal Conductivity at RT)

Two slabs of thickness L_1 and L_2 and thermal conductivities k_1 and k_2 are in thermal contact with each other, as shown in Figure 20.11. The temperatures of their outer surfaces are T_1 and T_2, respectively, and $T_2 > T_1$. Determine the temperature at the interface and the rate of energy transfer by conduction through the slabs in the steady-state condition.

$$\frac{k_1 A(T - T_1)}{L_1} = \frac{k_2 A(T_2 - T)}{L_2}$$

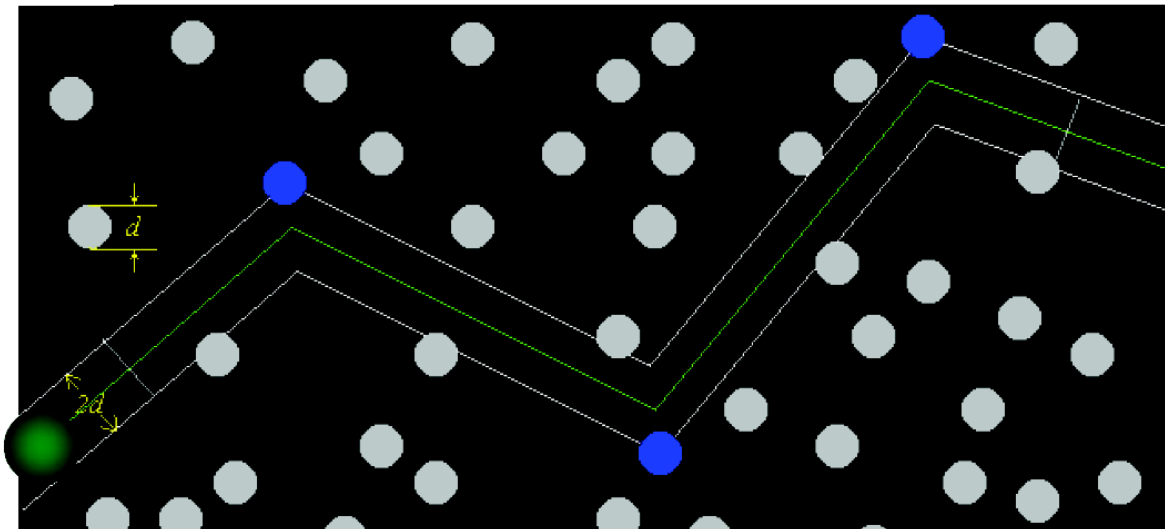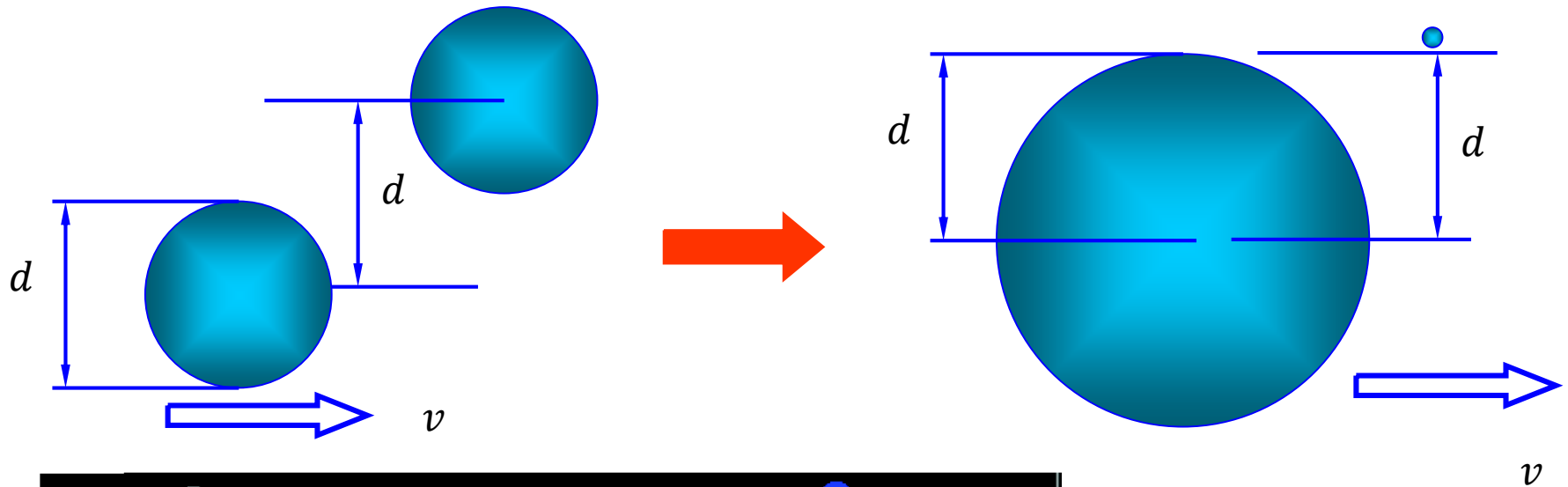$$T = \frac{k_1 L_2 T_1 + k_2 L_1 T_2}{k_1 L_2 + k_2 L_1}$$

$$\mathcal{P} = \frac{A(T_2 - T_1)}{(L_1/k_1) + (L_2/k_2)} = \frac{k_1 A(T - T_1)}{L_1} = \frac{k_2 A(T_2 - T)}{L_2}$$
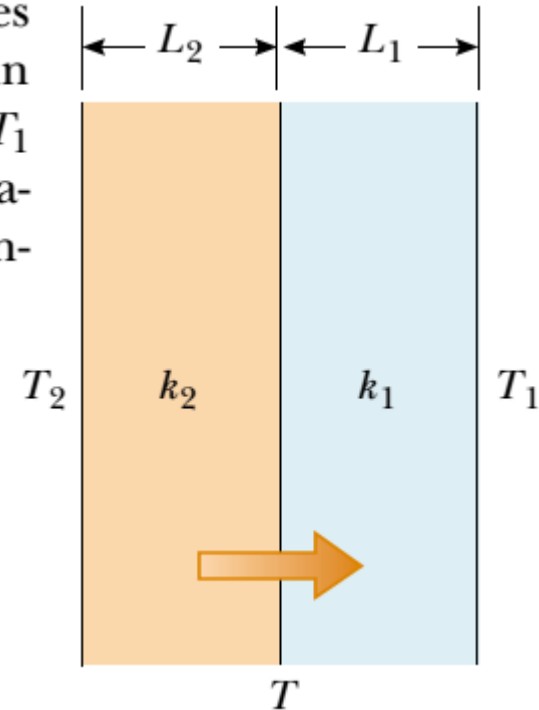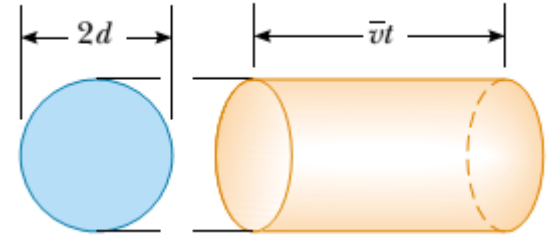
Mean Free Path

Average distance between two collisions

Mean Free Path

During time interval t, a molecule sweeps a cylinder of diameter 2d and length vt.

Volume of the cylinder

$$V = \pi d^2 \mathsf{v}t$$

Average number of collisions

$$z = n_V \pi d^2 \mathsf{v}t$$

Mean free path

$$l = \frac{\mathsf{v}t}{n_V \pi d^2 \mathsf{v}t} = \frac{1}{n_V \pi d^2} = \frac{k_B T}{\pi d^2 p}$$

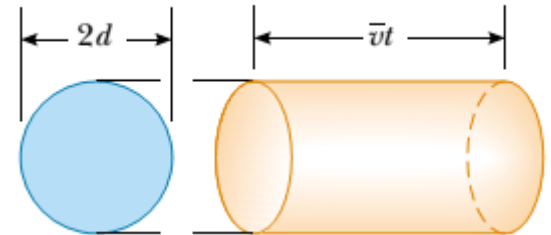$$p = n_V k_B T$$

$$n_V = p/(k_B T)$$

Mean Free Path

During time interval t, a molecule sweeps a cylinder of diameter 2d and length vt.

Average number of collisions

$$z = n_V \pi d^2 \text{vt}$$

Relative motion $v \rightarrow \sqrt{2}v$

Mean free path

$$l = \frac{\text{vt}}{n_V \pi d^2 (\sqrt{2}v)t} = \frac{1}{\sqrt{2}n_V \pi d^2} = \frac{k_B T}{\sqrt{2}\pi d^2 p}$$

Consider air at room temperature.

 – **How far does a typical molecule (with a diameter of 2 $\times 10^{-10}$ m) move before it collides with another molecule?**

$$n_V = \frac{N}{V} = \frac{P}{k_B T} = \frac{1.01 \times 10^5 \, \text{N/m}^2}{(1.38 \times 10^{-23} \, \text{J/K})(293 \, \text{K})}$$

$$= 2.50 \times 10^{25} \, \text{molecules/m}^3$$

Consider air at room temperature.

– **How far does a typical molecule (with a diameter of 2 ×10^{-10} m) move before it collides with another molecule?**

$$\ell = \frac{1}{\sqrt{2}\,\pi d^2 n_V}$$

$$= \frac{1}{\sqrt{2}\,\pi (2.00 \times 10^{-10}\ \text{m})^2 (2.50 \times 10^{25}\ \text{molecules/m}^3)}$$

$$= 2.25 \times 10^{-7}\ \text{m}$$

Q&A: Collision Frequency

Consider air at room temperature.

– **Average molecular separation:**

$$d = \frac{1}{n_V^{1/3}} = \frac{1}{(2.5 \times 10^{25})^{1/3}} = 3.4 \times 10^{-9} \text{ m}$$

$$\ell = \frac{1}{\sqrt{2}\,\pi d^2 n_V}$$

$$= \frac{1}{\sqrt{2}\,\pi(2.00 \times 10^{-10} \text{ m})^2(2.50 \times 10^{25} \text{ molecules/m}^3)}$$

$$= 2.25 \times 10^{-7} \text{ m}$$

Consider air at room temperature.

– On average, how frequently does one molecule collide with another?

$$\overline{v} = \sqrt{\frac{8kT}{\pi m}} \sim \sqrt{\frac{kT}{m}}$$

Expect ~ 500 m/s

$$f = \frac{\overline{v}}{l}$$

Expect ~ 2×10^9 /s

Try yourself!

Kinetic Theory*

Energy exchange across plane A

$$\longrightarrow \quad \mathbf{T}$$

$$Q = -\frac{1}{2}(U_R - U_L) = -\frac{1}{2} C_V \Delta T$$

U_L, N_L $\qquad$ U_R, N_R

$$\frac{f}{2}\left[\frac{N}{V}(\mathsf{A}l)\right]k_B \qquad\qquad \frac{\mathsf{d T}}{\mathsf{d x}}l$$

l $\qquad\qquad$ l
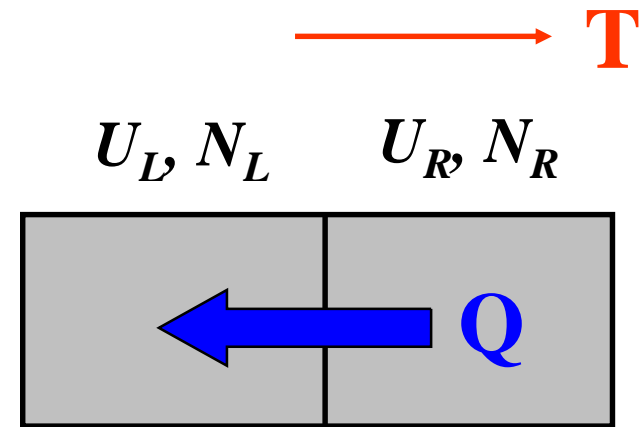
$$\frac{Q}{\Delta t} = -\kappa_t A \frac{\mathsf{d T}}{\mathsf{d x}}$$

$$\kappa_t = \frac{1}{2}\frac{f}{2}\frac{P}{T}l\,\mathsf{v_{th}} \xrightarrow{\;l \propto T\;} \gamma\sqrt{T} \qquad\qquad \gamma \sim \frac{f}{d_m^2}\frac{1}{\sqrt{m}}$$

From earlier lecture

$$l = 2.25 \times 10^{-7} \, m \qquad \overline{v} \approx 500 \text{ m/s}$$

$$\kappa_t = \frac{1}{2}\frac{f}{2}\frac{P}{T}\mathsf{l}\mathsf{v}_{\text{th}} = \frac{1}{2}\frac{5}{2}\frac{10^5 \text{N/m}}{300\text{K}} \cdot 2.25 \times 10^{-7} m \cdot 500\text{m/s}$$

$$= 0.047 \, \text{W}/(m \cdot K)$$

A factor less than 2 larger than the measured value of 0.026. Not bad after so many crude approximations.

Transport in Comparison

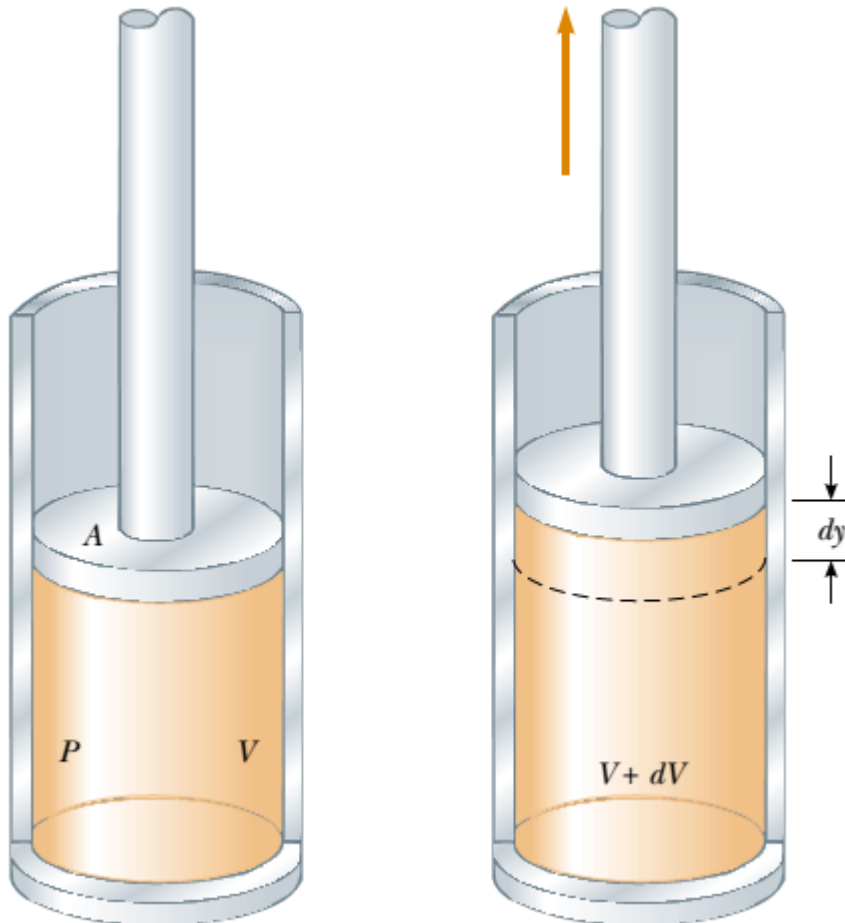| Phenomena	Imbalance	Things being transported	Experimental observation	Unit of Coefficient
Thermal conduction	temperature	energy	$\dfrac{Q}{\Delta t} = -\kappa_t A \dfrac{dT}{dx}$	W/m·K
Viscosity	velocity	momentum	$F = -\eta A \dfrac{dv}{dy}$	N·s/m²
Diffusion	density	particle	$I_x^{(n)} = -DA \dfrac{dn}{dx}$	m²/s
Charge conduction	voltage	charge	$I_x^{(e)} = -\sigma A \dfrac{dV}{dx}$	$\Omega^{-1}m^{-1}$

Internal Energy, Heat & Work

Heat is defined as the **transfer of energy** across the boundary of a system due to a **temperature difference** between the system and its surroundings.

Energy can also be transferred to or from the system by **work**.

Internal energy is all **the energy of a system** that is associated with its microscopic components — atoms and molecules — when viewed from a reference frame at rest with respect to the object.

Quasi-static assumption: the gas expands slowly enough to allow the system to remain essentially in thermal equilibrium at all times.

Work done by the gas
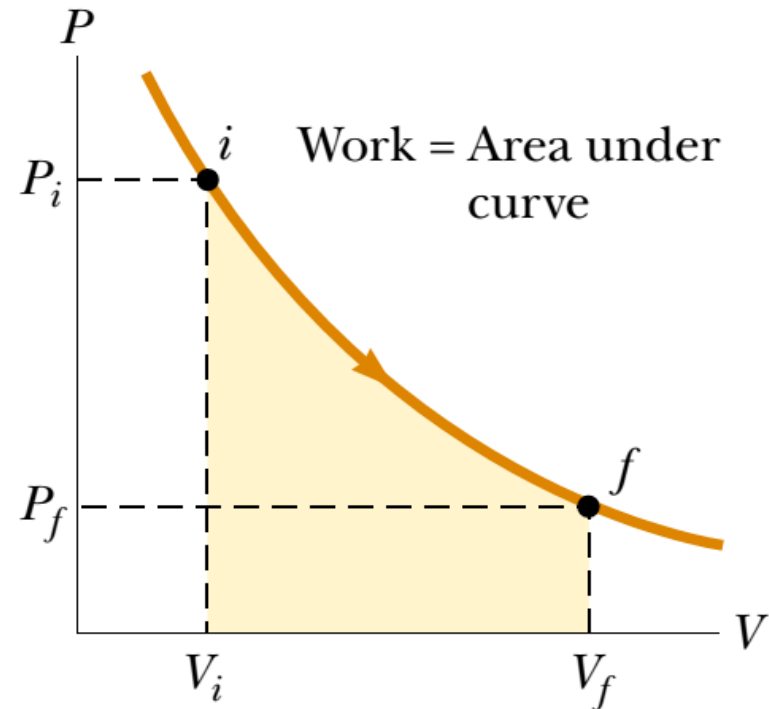
$$dW = Fdy = PAdy = PdV$$

$$W = \int PdV$$

Work in Thermodynamic Processes

Work done by the gas

$$dW = Fdy = PAdy = PdV$$

$$W = \int PdV$$

Work = Area under curve

The work done by a gas in the expansion from an initial state to a final state is the area under the curve connecting the states in a PV diagram.

Warning: Sign Convention

Historically, people are interested in the amount of work done by the expansion of gas, say, to drive a steam engine. The common treatment is

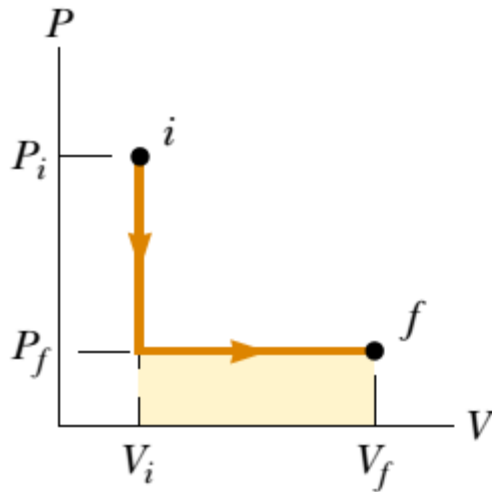– **Positive work: gas expands**

– **Negative work: gas compressed**

In mechanics we use the opposite sign, unfortunately.

But some books follow the same convention in thermal physics as in mechanics.
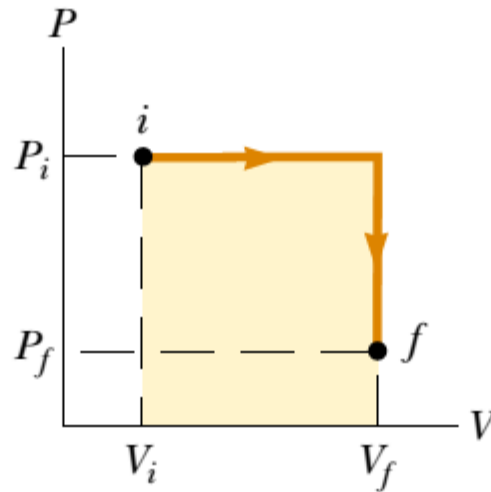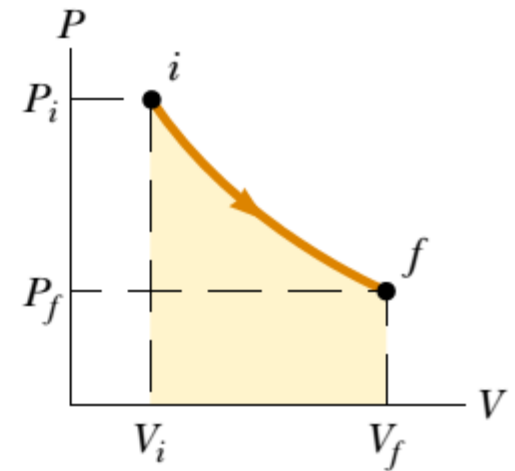
Trust your common sense!

Work Depends on the Path

(a)

(b)

(c)

$$W^{(a)} = P_f(V_f - V_i)$$

$$W^{(a)} < W^{(c)} < W^{(b)}$$

$$W^{(b)} = P_i(V_f - V_i)$$

The work done by a system depends on the initial, final, and intermediate states of the system.

Ideal Gases

Experiments found

$$pV = Nk_B T$$

Kinetic theory found

$$\overline{p}V = \frac{2N}{3}\overline{\frac{1}{2}mv^2}$$

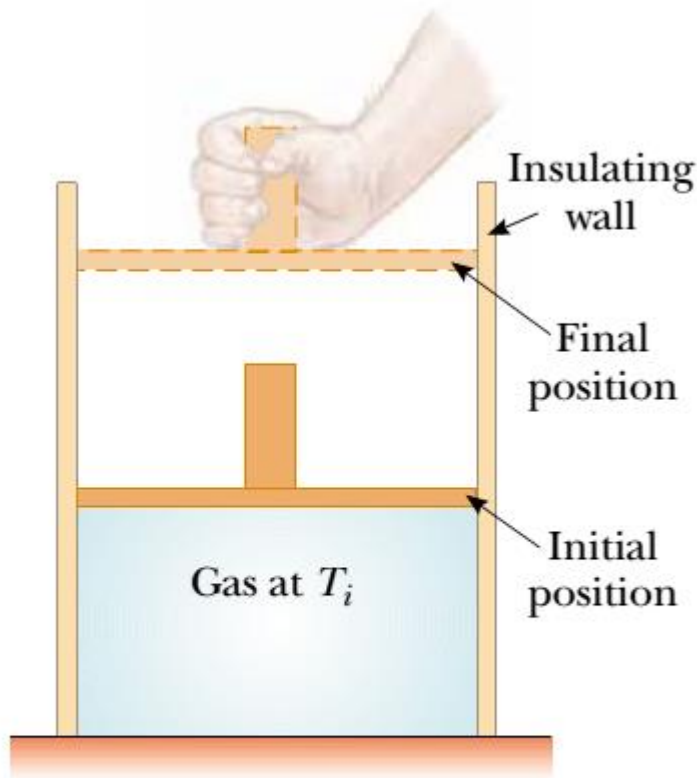$$\overline{\frac{1}{2}mv^2} = \frac{3}{2}k_B T$$

Generalized equipartition theorem (can be proved based on statistical principles)

$$U = N\frac{f}{2}k_B T \qquad \Longrightarrow \qquad C_V = \left(\frac{\Delta U}{\Delta T}\right)_{\text{fixed } V} = \frac{f}{2}Nk_B$$
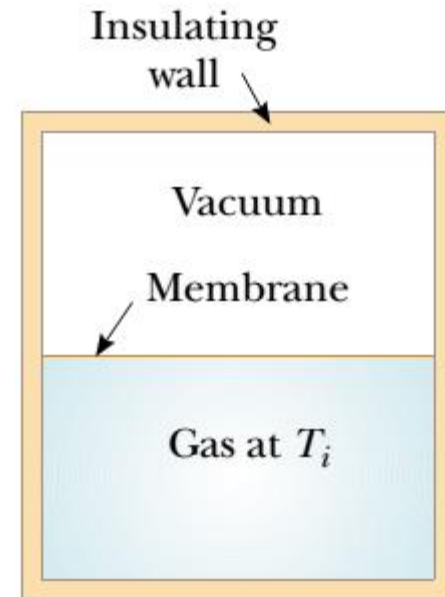
Isothermal vs Free Expansion

An adiabatic process is one during which no energy enters or leaves the system by heat.

Insulating wall

Final position

Initial position

Gas at T_i

Energy reservoir at T_i
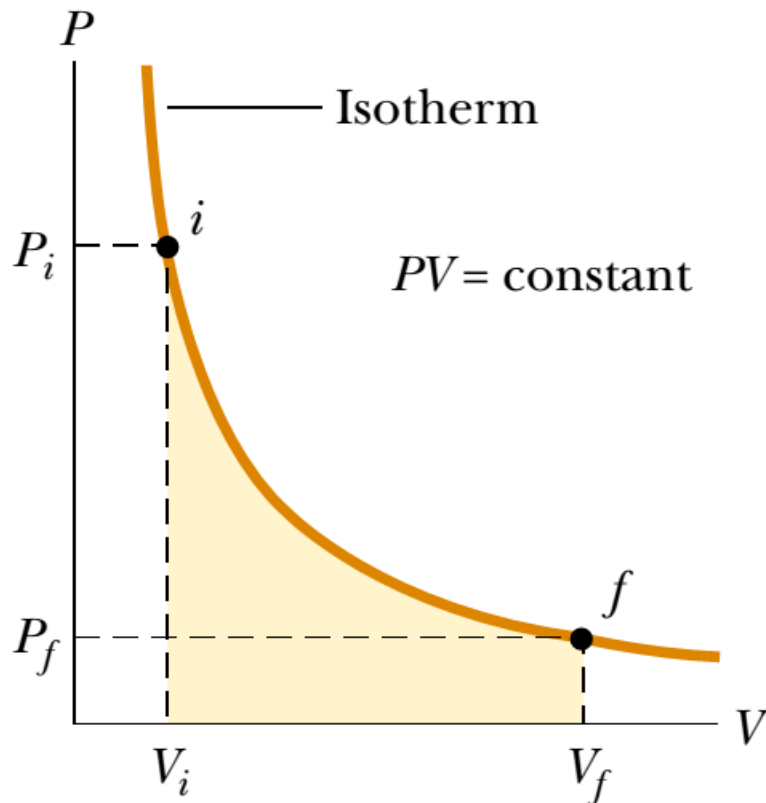
(a)

Insulating wall

Vacuum

Membrane

Gas at T_i

An energy reservoir is a source of energy that is considered to be so great that a finite transfer of energy from the reservoir does not change its temperature.

Isothermal Expansion

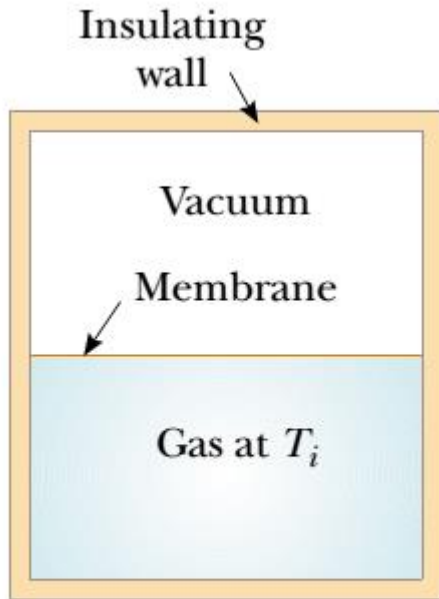$$W = \int PdV = \int \frac{Nk_B T}{V} dV = Nk_B T \ln \frac{V_f}{V_i}$$

$$\Delta U = 0 \qquad \text{at fixed } T$$

$$Q = W = Nk_B T \ln \frac{V_f}{V_i}$$

(Adiabatic) Free Expansion

Insulating wall

Vacuum

Membrane

Gas at T_i

(b)

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

Energy transfer by heat, like work done, depends on the initial, final, and intermediate states of the system.

- Is it possible to show the process on the PV diagram?
- Is the process reversible?

The 1st Law of Thermodynamics

Although Q and W both depend on the path, the quantity Q-W is independent of the path change.

The change in the internal energy U of the system can be expressed as:

$$\Delta U = Q - W$$

The infinitesimal change:

$$dU = \bar{d}Q - PdV$$

reminding you that it is path dependent
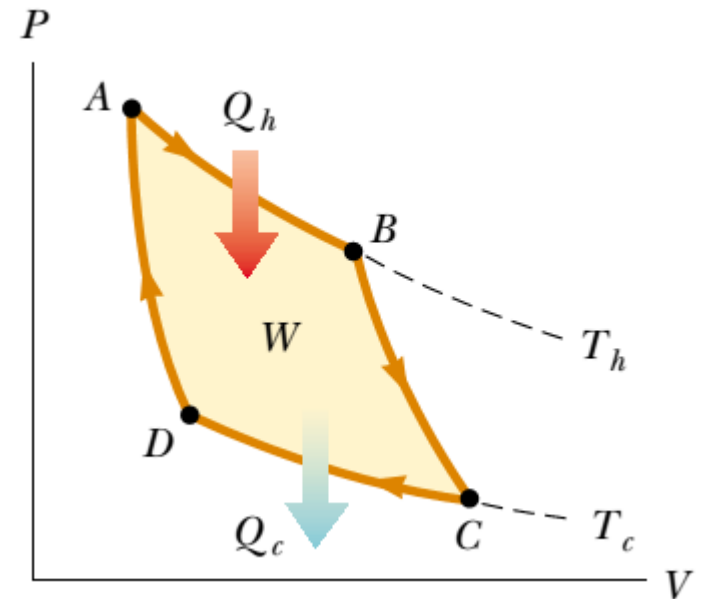
Discussion on the 1st Law

The 1st law is a statement of energy conservation (now with the internal energy included).

The internal energy of an *isolated system* remains constant.

In a *cyclic process*,

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

– The net work done by the system per cycle equals the area enclosed by the path representing the process on a PV diagram.

Discussion on the 1st Law

On a microscopic scale, no distinction exists between the result of heat and that of work.

The internal energy function is therefore called a *state function*, whose value is determined by the state of the system.

– In general,

$$U = U(T, V)$$

If we take energy and volume as parameters, how comes heat is path dependent?

$$\bar{d}Q = dU + PdV$$

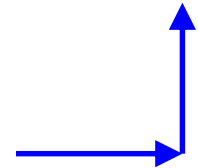**In mathematical language, $dU + pdV$ is an *inexact differential*.**

- In multivariate calculus, a differential is said to be exact (or perfect), as contrasted with an inexact differential, if it is of the form dQ, for some differentiable function Q.
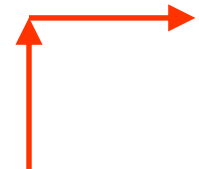
Assume $$\bar{d}g = dx + \frac{x}{y}dy$$

$$\left(\int_{(1,1)}^{(2,1)} + \int_{(2,1)}^{(2,2)}\right)\left(dx + \frac{x}{y}dy\right) = 1 + 2\ln 2$$

$$\left(\int_{(1,1)}^{(1,2)} + \int_{(1,2)}^{(2.2)}\right)\left(dx + \frac{x}{y}dy\right) = \ln 2 + 1$$

Note: $df \equiv \dfrac{\bar{d}g}{x} = \dfrac{dx}{x} + \dfrac{dy}{y}$ **is an exact differential.**

Integrating factor
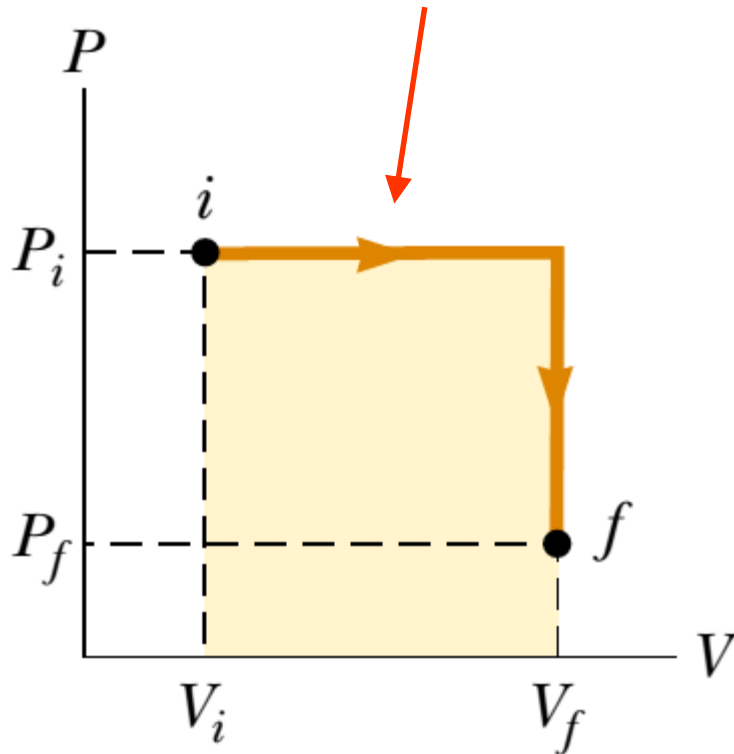
$$f(x,y) = \ln x + \ln y + f_0$$

Isobaric Processes

isobaric

$$W = P(V_f - V_i) \qquad \Delta U = C_V \Delta T$$

$$Q = \Delta U + W = C_V \Delta T + P\Delta V$$

$$\xrightarrow{\text{PV=Nk}_B T} C_V \Delta T + \text{Nk}_B \Delta T$$

$$C_P = \left(\frac{Q}{\Delta T}\right)_{\text{fixed } P} = C_V + \text{Nk}_B$$

$$C_V = (f/2)\text{Nk}_B \Rightarrow \gamma = C_P/C_V = \frac{f+2}{f}$$
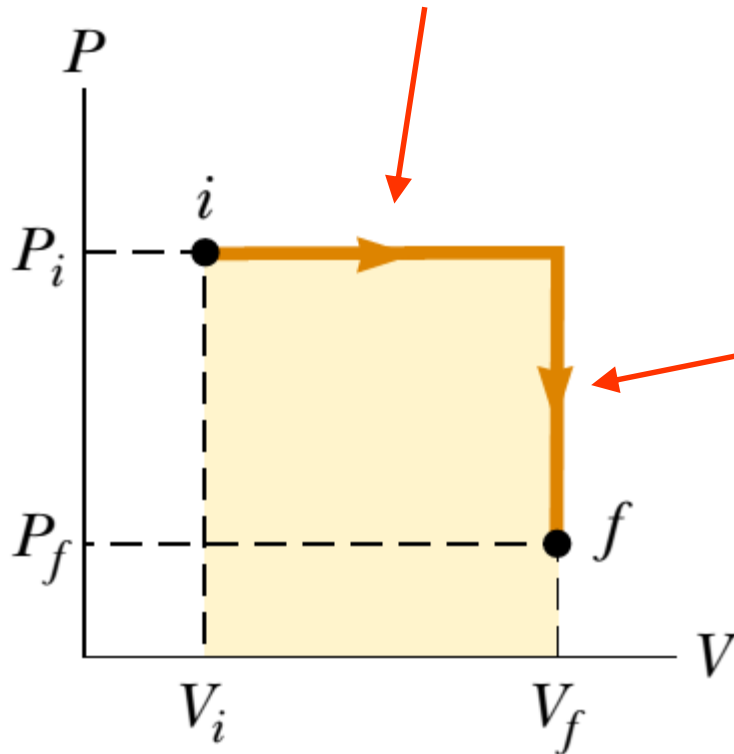
Isobaric vs Isovolumetric Processes

isobaric

$$W = P(V_f - V_i)$$

$$\Delta U = C_V \Delta T$$

$$Q = \Delta U + W = C_P \Delta T$$

isovolumetric

$$W = 0$$

$$\Delta U = C_V \Delta T$$

$$Q = \Delta U = C_V \Delta T$$

Molar specific heat: $C_P == C_V + R$

Degrees of Freedom, Again

TABLE 21.2 **Molar Specific Heats of Various Gases**

Gas	Molar Specific Heat (J/mol · K)[a]			
	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

$$C_V = \frac{f}{2} Nk_B$$

$$C_P = \frac{f+2}{2} Nk_B$$

$$\gamma = C_P/C_V = \frac{f+2}{f}$$

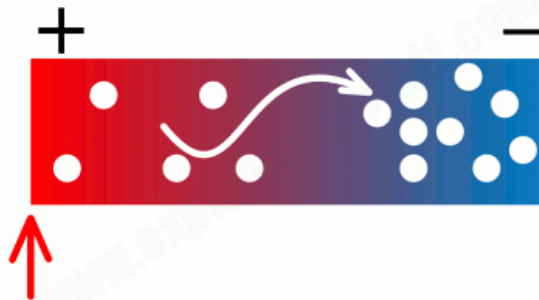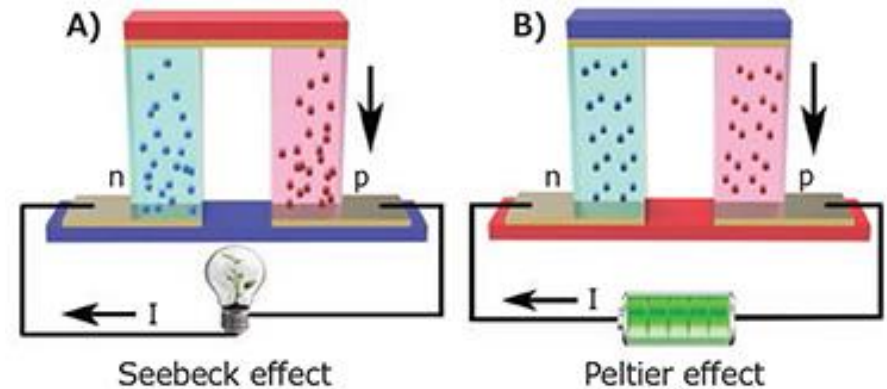| f	3	5	7
γ	1.67	1.4	1.28

Thermoelectric effect*

- Seebeck Effect and Thermopower:

$$\mathbf{E} = Q\nabla T,$$

$$Q = -\frac{\pi^2}{6}\frac{k_B}{e}\left(\frac{k_B T}{\varepsilon_F}\right) = -1.42\left(\frac{k_B T}{\varepsilon_F}\right) \times 10^{-4} \text{ volt/K},$$

www.explainthatstuff.com

Seebeck effect

Peltier effect

https://www.bilibili.com/video/BV1is41177Ld/?spm_id_from=333.788.videocard.2

https://www.bilibili.com/video/BV1Yt411G7Up?from=search&seid=10049906192156826855