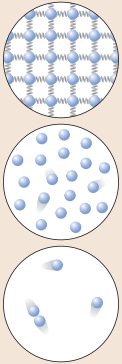
The goal of Chapter 16 has been to learn the characteristics of macroscopic systems.

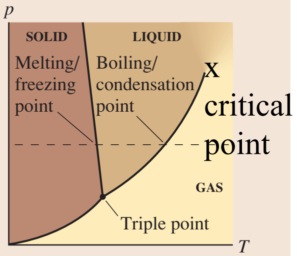
General Principles

Three Common Phases of Matter

Solid	Rigid, definite shape. Nearly incompressible.
Liquid	Molecules loosely held together by molecular bonds, but able to move around. Nearly incompressible.
Gas	Molecules moving freely through space. Compressible.



The different phases exist for different conditions of temperature T and pressure p. The boundaries separating the regions of a phase diagram are lines of phase equilibrium. Any amounts of the two phases can coexist in equilibrium. The **triple point** is the one value of temperature and pressure at which all three phases can coexist in equilibrium.

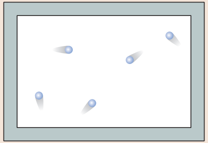


for water; usually solid-liquid line tilts to higher, not lower T

Important Concepts

$$A = \#\text{ protons} + \#\text{ neutrons} \qquad M_{\text{mol}} = A\text{ gm}$$

Ideal-Gas Model



- Atoms and molecules are small, hard spheres that travel freely through space except for occasional collisions with each other or the walls.
- The model is valid when the density is low and the temperature well above the condensation point.

Ideal-Gas Law

The **state variables** of an ideal gas are related by the ideal-gas law

$$pV = nRT \quad \text{or} \quad pV = Nk_BT$$

where $R = 8.31$ J/mol K is the universal gas constant and $k_B = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. p, V, and T *must* be in SI units of Pa, m^3, and K.

$$R = N_A k_B$$

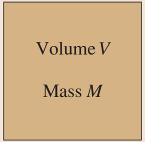
For a gas in a sealed container, with constant n:

$$\frac{p_2V_2}{T_2} = \frac{p_1V_1}{T_1}$$

Counting atoms and moles

A macroscopic sample of matter consists of N atoms (or molecules), each of mass m (the **atomic** or **molecular mass**):

$$N = \frac{M}{m}$$



Alternatively, we can state that the sample consists of n **moles:**

$$n = \frac{N}{N_A} \quad \text{or} \quad \frac{M}{M_{\text{mol}}}$$

where $N_A = 6.02 \times 10^{23}$ mol^{-1} is **Avogadro's number.**

The molar mass M_{mol}, in kg/mol, is the numerical value of the atomic or molecular mass in u divided by 1000. The atomic or molecular mass, in atomic mass units u, is well approximated by the **atomic mass number** A. The atomic mass unit is

$$1\text{ u} = 1.66 \times 10^{-27}\text{ kg}$$

The **number density** of the sample is $\frac{N}{V}$.

$$N_A\,\text{u} = 1\text{ gm}$$

Applications

Temperature scales

$$T_F = \frac{9}{5}T_C + 32^\circ \qquad T_K = T_C + 273$$

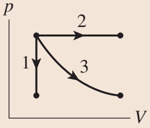
The Kelvin temperature scale is based on:

- Absolute zero at $T_0 = 0$ K
- The triple point of water at $T_3 = 273.16$ K

Three basic gas processes

1. **Isochoric,** or constant volume
2. **Isobaric,** or constant pressure
3. **Isothermal,** or constant temperature

pV diagram



The goal of Chapter 17 has been to develop and apply the first law of thermodynamics.

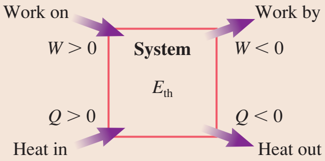
General Principles

First Law of Thermodynamics

$$\Delta E_{\text{th}} = W_{\text{on}} + Q \quad = Q - W_{\text{by}}$$

The first law is a general statement of energy conservation.

Work W and heat Q depend on the process by which the system is changed.



The change in the system depends only on the total energy exchanged $W + Q$, not on the process.

Energy

Thermal energy E_{th} Microscopic energy of moving molecules and stretched molecular bonds. ΔE_{th} depends on the initial/final states but is independent of the process.

Work W Energy transferred to the system by forces in a mechanical interaction.

Heat Q Energy transferred to the system via atomic-level collisions when there is a temperature difference. A thermal interaction.

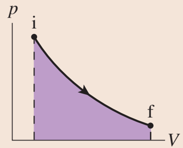
Important Concepts

The **work** done on a gas is

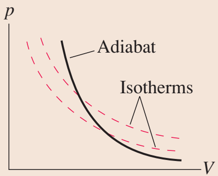
$$W = -\int_{V_i}^{V_f} p\,dV$$

$$= -(\text{area under the } pV \text{ curve})$$

$$W_{by} = + \text{area under pV curve}$$



An **adiabatic process** is one for which $Q = 0$. Gases move along an **adiabat** for which $pV^{\gamma} =$ constant, where $\gamma = C_P/C_V$ is the **specific heat ratio.** An adiabatic process changes the temperature of the gas without heating it.



Calorimetry When two or more systems interact thermally, they come to a common final temperature determined by

$$Q_{net} = Q_1 + Q_2 + \cdots = 0$$

The heat of transformation L is the energy needed to cause 1 kg of substance to undergo a phase change

$$Q = \pm ML$$

The specific heat c of a substance is the energy needed to raise the temperature of 1 kg by 1 K:

$$Q = Mc\Delta T$$

The molar specific heat C is the energy needed to raise the temperature of 1 mol by 1 K:

$$Q = nC\Delta T$$

The molar specific heat of gases depends on the *process* by which the temperature is changed:

C_V = molar specific heat at **constant volume**

$C_P = C_V + R$ = molar specific heat at **constant pressure**

Heat is transferred by **conduction, convection, radiation,** and **evaporation.**

Conduction: $Q/\Delta t = (kA/L)\Delta T$

Radiation: $Q/\Delta t = e\sigma AT^4$

Summary of Basic Gas Processes

Process	Definition	Stays constant	Work $=W_{on} = -W_{by}$	Heat
Isochoric	$\Delta V = 0$	V and p/T	$W = 0$	$Q = nC_V \Delta T$
Isobaric	$\Delta p = 0$	p and V/T	$W = -p\Delta V$	$Q = nC_P \Delta T$
Isothermal	$\Delta T = 0$	T and pV	$W = -nRT \ln(V_f/V_i)$	$\Delta E_{th} = 0$
Adiabatic	$Q = 0$	pV^γ or $TV^{\gamma-1}$	$W = \Delta E_{th}$	$Q = 0$
All gas processes	First law $\Delta E_{th} = W + Q = nC_V \Delta T$		Ideal-gas law $pV = nRT$	

$= Q - W_{by}$

The goal of Chapter 18 has been to understand a macroscopic system in terms of the microscopic behavior of its molecules.

General Principles

The **micro/macro connection** relates the macroscopic properties of a system to the motion and collisions of its atoms and molecules.

The Equipartition Theorem

Tells us how collisions distribute the energy in the system. The energy stored in each mode of the system (each **degree of freedom**) is $\frac{1}{2}Nk_BT$ or, in terms of moles, $\frac{1}{2}nRT$.

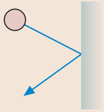
The Second Law of Thermodynamics

Tells us how collisions move a system toward equilibrium. The entropy of an isolated system can only increase or, in equilibrium, stay the same.

- Order turns into disorder and randomness.
- Systems run down.
- Heat energy is transferred spontaneously from a hotter to a colder system, never from colder to hotter.

Important Concepts

$\lambda \sim (N/V)^{-1} r^{-2}$

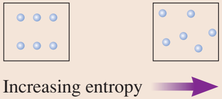


Pressure is due to the force of the molecules colliding with the walls:

$$p = \frac{1}{3}\frac{N}{V} m {v_{\mathrm{rms}}}^2 = \frac{2}{3}\frac{N}{V}\epsilon_{\mathrm{avg}}$$

The **average translational kinetic energy** of a molecule is $\epsilon_{\mathrm{avg}} = \frac{3}{2}k_B T$. The temperature of the gas $T = \frac{2}{3k_B}\epsilon_{\mathrm{avg}}$ measures the average translational kinetic energy.

Entropy measures the probability that a macroscopic state will occur or, equivalently, the amount of disorder in a system.

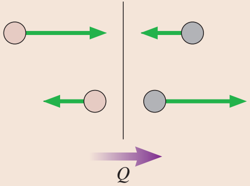


The **thermal energy** of a system is

E_{th} = translational kinetic energy + rotational kinetic energy + vibrational energy

- **Monatomic gas** $E_{\mathrm{th}} = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$
- **Diatomic gas** $E_{\mathrm{th}} = \frac{5}{2}Nk_B T = \frac{5}{2}nRT$ at moderate T
- **Elemental solid** $E_{\mathrm{th}} = 3Nk_B T = 3nRT$

Heat is energy transferred via collisions from more-energetic molecules on one side to less-energetic molecules on the other. Equilibrium is reached when $(\epsilon_1)_{\mathrm{avg}} = (\epsilon_2)_{\mathrm{avg}}$, which implies $T_{1\mathrm{f}} = T_{2\mathrm{f}}$.



Applications

The root-mean-square speed v_{rms} is the square root of the average of the squares of the molecular speeds:

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}}$$

For molecules of mass m at temperature T, $v_{\text{rms}} = \sqrt{\dfrac{3k_{\text{B}}T}{m}}$

Molar specific heats can be predicted from the thermal energy because $\Delta E_{\text{th}} = nC\Delta T$.

- **Monatomic gas** $C_{\text{V}} = \frac{3}{2}R$
- **Diatomic gas** $C_{\text{V}} = \frac{5}{2}R$ at moderate T
- **Elemental solid** $C = 3R$

Terms and Notation

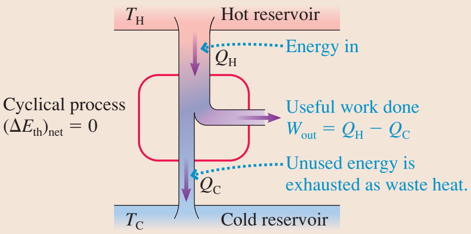
histogram
mean free path, λ
root-mean-square speed, v_{rms}
degrees of freedom
equipartition theorem
irreversible process
entropy
second law of thermodynamics

The goal of Chapter 19 has been to study the physical principles that govern heat engines and refrigerators.

General Principles

Heat Engines

Devices that transform heat into work. They require two energy reservoirs at different temperatures.



Energy in

Useful work done $W_{out} = Q_H - Q_C$

Unused energy is exhausted as waste heat.

Thermal efficiency

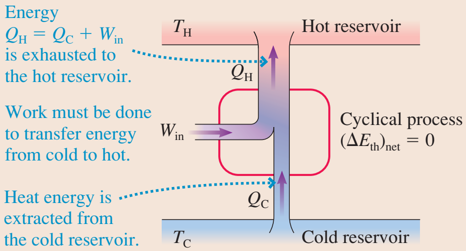
$$\eta = \frac{W_{out}}{Q_H} = \frac{\text{what you get}}{\text{what you pay}}$$

Second-law limit:

$$\eta \le 1 - \frac{T_C}{T_H}$$

Refrigerators

Devices that use work to transfer heat from a colder object to a hotter object.



Energy $Q_H = Q_C + W_{in}$ is exhausted to the hot reservoir.

Work must be done to transfer energy from cold to hot.

Heat energy is extracted from the cold reservoir.

Coefficient of performance

$$K = \frac{Q_C}{W_{in}} = \frac{\text{what you get}}{\text{what you pay}}$$

Second-law limit:

$$K \le \frac{T_C}{T_H - T_C}$$

Important Concepts

A perfectly reversible engine (a **Carnot engine**) can be operated as either a heat engine or a refrigerator between the same two energy reservoirs by reversing the cycle and with no other changes.

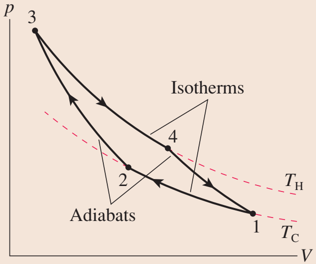
- A **Carnot heat engine** has the maximum possible thermal efficiency of any heat engine operating between T_H and T_C:

$$\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$

- A **Carnot refrigerator** has the maximum possible coefficient of performance of any refrigerator operating between T_H and T_C:

$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C}$$

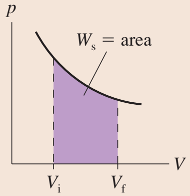
The Carnot cycle for a gas engine consists of two isothermal processes and two adiabatic processes.



An energy reservoir is a part of the environment so large in comparison to the system that its temperature doesn't change as the system extracts heat energy from or exhausts heat energy to the reservoir. All heat engines and refrigerators operate between two energy reservoirs at different temperatures T_H and T_C.

The **work** W_s done *by* the system has the opposite sign to the work done *on* the system.

W_s = area under pV curve



Applications

To analyze a heat engine or refrigerator:

MODEL Identify each process in the cycle.

VISUALIZE Draw the pV diagram of the cycle.

SOLVE There are several steps:

- Determine p, V, and T at the beginning and end of each process.
- Calculate ΔE_{th}, W_{s}, and Q for each process.
- Determine W_{in} or W_{out}, Q_{H}, and Q_{C}.
- Calculate $\eta = W_{\text{out}}/Q_{\text{H}}$ or $K = Q_{\text{C}}/W_{\text{in}}$.

ASSESS Verify $(\Delta E_{\text{th}})_{\text{net}} = 0$. Check signs.

KNOWLEDGE STRUCTURE IV Thermodynamics

ESSENTIAL CONCEPTS Work, heat, and thermal energy

BASIC GOALS How is energy converted from one form to another?
How are macroscopic properties related to microscopic behavior?

GENERAL PRINCIPLES

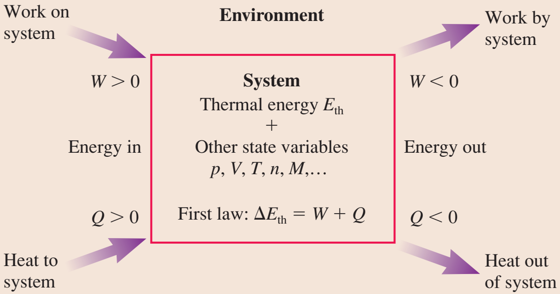
First law of thermodynamics Energy is conserved, $\Delta E_{\text{th}} = W + Q$.

Second law of thermodynamics Heat is not spontaneously transferred from a colder object to a hotter object.

GAS LAWS AND PROCESSES Ideal-gas law $pV = nRT = Nk_{\text{B}}T$

- Isochoric process V = constant and $W = 0$
- Isothermal process T = constant and $\Delta E_{\text{th}} = 0$
- Isobaric process p = constant
- Adiabatic process $Q = 0$

Energy Transformation



Work

Requires volume change

Gas: $W = -\int p\,dV$

$= -$(area under pV curve)

Thermal Energy

$E_{\text{th}} = \frac{1}{2}Nk_{\text{B}}T$ per degree of freedom

Heat

Requires temperature difference

$Q = Mc\Delta T$ or $nC\Delta T$

$Q = \pm ML$ for phase changes

Heat Engines

$$W_{\text{out}} = \text{area inside } pV \text{ curve}$$
$$= Q_{\text{H}} - Q_{\text{C}}$$

$$\eta = \frac{W_{\text{out}}}{Q_{\text{H}}}$$

$$\eta_{\max} = \eta_{\text{Carnot}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}$$