Chapter 19

The Kinetic Theory of Gases

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19-1 Avogadro's Number

Learning Objectives

19.01 Identify Avogadro's number N_A.

19.02 Apply the relationship between the number of moles n, the number of molecules N, and Avogadro's number N_A.

19.03 Apply the relationships between the mass m of a sample, the molar mass M of the molecules in the sample, the number of moles n in the sample, and Avogadro's number N_A.

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19-1 Avogadro's Number

The **kinetic theory of gases** relates the macroscopic properties of gases to the microscopic properties of gas molecules.

One **mole** of a substance contains N_A (**Avogadro's number**) elementary units (usually atoms or molecules), where N_A is found experimentally to be $N_A = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$

The mass per mole M of a substance is related to the mass *m* of an individual molecule of the substance by $M = mN_A$

The number of moles n contained in a sample of mass M_{sam}, consisting of *N* molecules, is related to the molar mass M of the molecules and to Avogadro's number N_A as given by

$$n = \frac{M_{\mathrm{sam}}}{M} = \frac{M_{\mathrm{sam}}}{mN_{\mathrm{A}}}.$$

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19-2 Ideal Gases

Learning Objectives

19.04 Identify why an ideal gas is said to be ideal.

19.05 Apply either of the two forms of the ideal gas law, written in terms of the number of moles *n* or the number of molecules *N*.

19.06 Relate the ideal gas constant R and the Boltzmann constant k.

19.07 Identify that the temperature in the ideal gas law must be in kelvins.

19.08 Sketch *p*-*V* diagrams for a constant-temperature expansion of a gas and a constant-temperature contraction.

19.09 Identify the term isotherm.

19.10 Calculate the work done by a gas, including the algebraic sign, for an expansion and a contraction along an isotherm.

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Learning Objectives (Continued)

19.11 For an isothermal process, identify that the change in internal energy ΔE is zero and that the energy Q transferred as heat is equal to the work W done.

19.12 On a p-V diagram, sketch a constant-volume process and identify the amount of work done in terms of area on the diagram.

19.13 On a p-V diagram, sketch a constant-pressure process and determine the work done in terms of area on the diagram.

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19-2 Ideal Gases

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

$$pV = nRT$$

Here *n* is the number of moles of the gas present and R is a constant (8.31 J/mol.K) called the gas constant.

The Second Expression for the law is:

$$pV = NkT$$

where *k* is the Boltzmann constant

(*a*)

(*b*)

Courtesy www.doctorslime.com

Large steel tank crushed by atmospheric pressure. A dramatic example of ideal gas law

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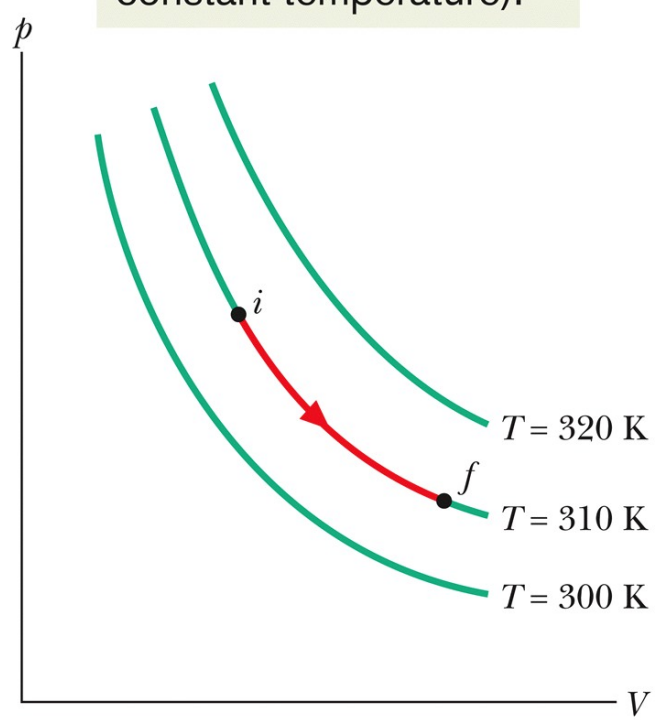
19-2 Ideal Gases

The work done by an ideal gas during an isothermal (constant-temperature) change from volume V_i to volume V_f is

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

Three isotherms on a *p-V* diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state *i* to a final state *f*. The path from *f* to *i* along the isotherm would represent the reverse process — that is, an isothermal compression.

The expansion is along an isotherm (the gas has constant temperature).



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19-3 Pressure, Temperature, and rms Speed

Learning Objectives

19.14 Identify that the pressure on the interior walls of a gas container is due to the molecular collisions with the walls.

19.15 Relate the pressure on a container wall to the momentum of the gas molecules and the time intervals between their collisions with the wall.

19.16 For the molecules of an ideal gas, relate the root-mean-square speed v_{rms} and the average speed v_{avg}.

19.17 Relate the pressure of an ideal gas to the *rms* speed v_{rms} of the molecules.

19.18 For an ideal gas, apply the relationship between the gas temperature T and the *rms* speed v_{rms} and molar mass M of the molecules.

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19-3 Pressure, Temperature, and rms Speed

In terms of the speed of the gas molecules, the pressure exerted by *n* moles of an ideal gas is

$$p = \frac{nMv_{\text{rms}}^2}{3V},$$

where $v_{rms} = 2\sqrt{(v^2)_{avg}}$ is the root-mean-square speed of the molecules, M is the molar mass, and V is the volume.

The *rms* speed can be written in terms of the temperature as

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}.$$

Table 19-1 Some RMS Speeds at Room Temperature ($T = 300$ K)[a]

Gas	Molar Mass (10^{-3} kg/mol)	v_{rms} (m/s)
Hydrogen (H_2)	2.02	1920
Helium (He)	4.0	1370
Water vapor (H_2O)	18.0	645
Nitrogen (N_2)	28.0	517
Oxygen (O_2)	32.0	483
Carbon dioxide (CO_2)	44.0	412
Sulfur dioxide (SO_2)	64.1	342

[a]For convenience, we often set room temperature equal to 300 K even though (at 27°C or 81°F) that represents a fairly warm room.

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19-4 Translational Kinetic Energy

Learning Objectives

19.19 For an ideal gas, relate the average kinetic energy of the molecules to their rms speed.

19.20 Apply the relationship between the average kinetic energy and the temperature of the gas.

19.21 Identify that a measurement of a gas temperature is effectively a measurement of the average kinetic energy of the gas molecules.

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19-4 Translational Kinetic Energy

The **average translational kinetic energy** is related to the temperature of the gas:

$$K_{avg} = \tfrac{3}{2}kT.$$

At a given temperature T, all ideal gas molecules—no matter what their mass—have the same average translational kinetic energy—namely, $\frac{3}{2}kT$. When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

Checkpoint 2

A gas mixture consists of molecules of types 1, 2, and 3, with molecular masses $m_1 > m_2 > m_3$. Rank the three types according to (a) average kinetic energy and (b) rms speed, greatest first.

Answer: (a) 1=2=3 (b) 3,2 and 1

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19-7 The Molar Specific Heats of an Ideal Gas

Learning Objectives

19.28 Identify that the internal energy of an ideal monatomic gas is the sum of the translational kinetic energies of its atoms.

19.29 Apply the relationship between the internal energy E_{int} of a monatomic ideal gas, the number of moles n, and the gas temperature T.

19.30 Distinguish between monatomic, diatomic, and polyatomic ideal gases.

19.31 For monatomic, diatomic, and polyatomic ideal gases, evaluate the molar specific heats for a constant-volume process and a constant-pressure process.

19.32 Calculate a molar specific heat at constant pressure C_p by adding R to the molar specific heat at constant volume C_V, and explain why (physically) C_p is greater.

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19-7 The Molar Specific Heats of an Ideal Gas

Learning Objectives (Continued)

19.33 Identify that the energy transferred to an ideal gas as heat in a constant-volume process goes entirely into the internal energy but that in a constant-pressure process energy also goes into the work done to expand the gas.

19.34 Identify that for a given change in temperature, the change in the internal energy of an ideal gas is the same for any process and is most easily calculated by assuming a constant-volume process.

19.35 For an ideal gas, apply the relationship between heat Q, number of moles n, and temperature change ΔT, using the appropriate molar specific heat.

19.36 Between two isotherms on a p-V diagram, sketch a constant-volume process and a constant-pressure process, and for each identify the work done in terms of area on the graph.

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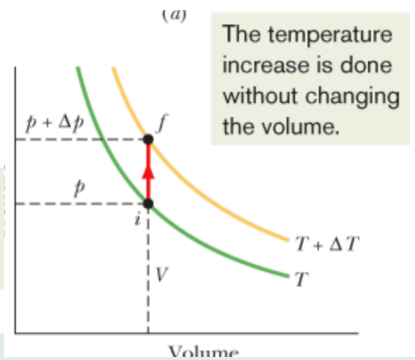
Molar specific heat at constant volume derivation

$$E_{int} = (nN_A)K_{avg} = (nN_A)(\tfrac{3}{2}kT) .$$

Using Eq. 19-7 ($k = R/N_A$), we can rewrite this as

$$E_{int} = \frac{3}{2}nRT \quad \text{(monatomic ideal gas)} .$$



The internal energy E_{int} of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

$$Q = nC_V\Delta T \quad \text{(constant volume)}, \tag{19-39}$$

where C_V is a constant called the **molar specific heat at constant volume**. Substituting this expression for Q into the first law of thermodynamics as given by Eq. 18-26 ($\Delta E_{int} = Q - W$) yields

$$\Delta E_{int} = nC_V\Delta T - W . \tag{19-40}$$

With the volume held constant, the gas cannot expand and thus cannot do any work. Therefore, $W = 0$, and Eq. 19-40 gives us

$$C_V = \frac{\Delta E_{int}}{n\Delta T} . \tag{19-41}$$

From Eq. 19-38, the change in internal energy must be

$$\Delta E_{int} = \frac{3}{2}nR\Delta T . \tag{19-42}$$

Substituting this result into Eq. 19-41 yields

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K} \quad \text{(monatomic gas)} . \tag{19-43}$$

$$E_{\text{int}} = nC_V T \quad \text{(any ideal gas)} .$$

monatomic gas but also to diatomic and polyatomic i
the internal energy of a gas depends on the temperatu
perature change ΔT, then from either Eq. 19-41 or E

$$\Delta E_{\text{int}} = nC_V \Delta T \quad \text{(ideal gas, any process)} .$$

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Molar specific heat at constant pressure derivation

$$Q = nC_p \Delta T \quad \text{(constant pressure)},$$

$$\Delta E_{\text{int}} = Q - W .$$

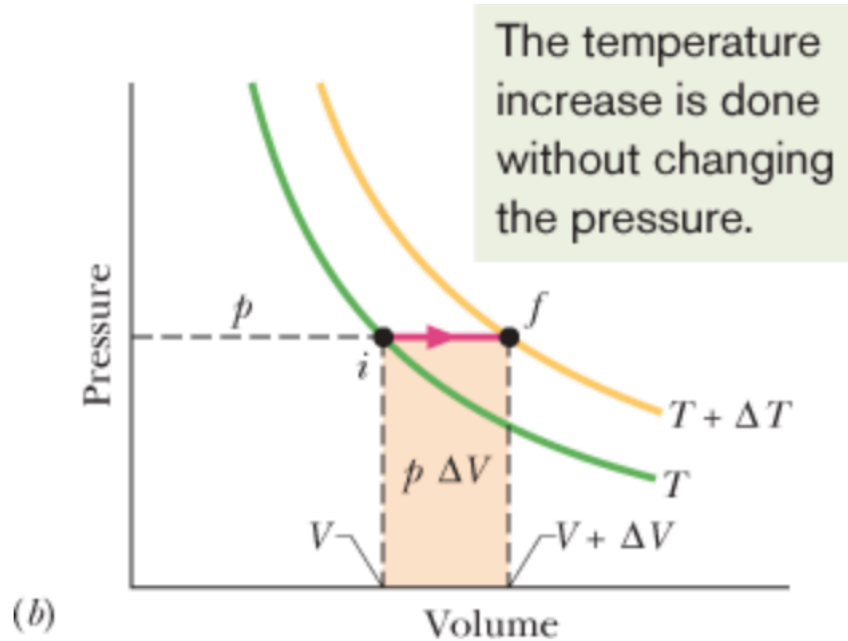
e substitute from Eq. 19-45. For
ls us that $W = p\,\Delta V$. Then we n

$$W = p\,\Delta V = nR\,\Delta T .$$

ding through by $n\,\Delta T$, we find

$$C_V = C_p - R$$

$$C_p = C_V + R .$$



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19-7 The Molar Specific Heats of an Ideal Gas

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19.37 Calculate the work done by an ideal gas for a constant-pressure process.

19.38 Identify that work is zero for constant volume.

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19-7 The Molar Specific Heats of an Ideal Gas

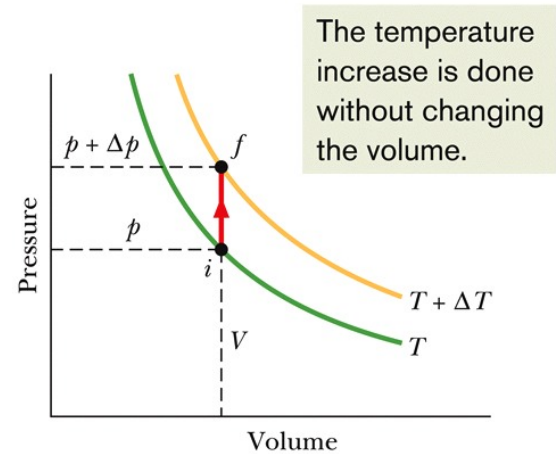
Molar Specific Heat at Constant Volume

The internal energy E_{int} of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

$$E_{int} = \tfrac{3}{2}nRT$$

The **molar specific heat** of a gas at **constant volume** is defined to be

$$Q = nC_V \Delta T$$



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A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, *not* on what type of process produces the change.

$$\Delta E_{int} = nC_V \Delta T$$

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19-7 The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Pressure

The **molar specific heat** of a gas at **constant pressure** is defined to be

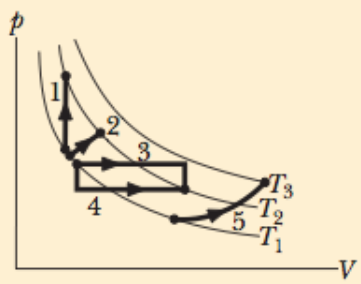
$$C_p = \frac{Q}{n\,\Delta T}$$

where C_p can also be defined as

$$C_p = C_V + R.$$

Checkpoint 4

The figure here shows five paths traversed by a gas on a p-V diagram. Rank the paths according to the change in internal energy of the gas, greatest first.



Answer: 5 and then—4,3,2,1—with same int. energy

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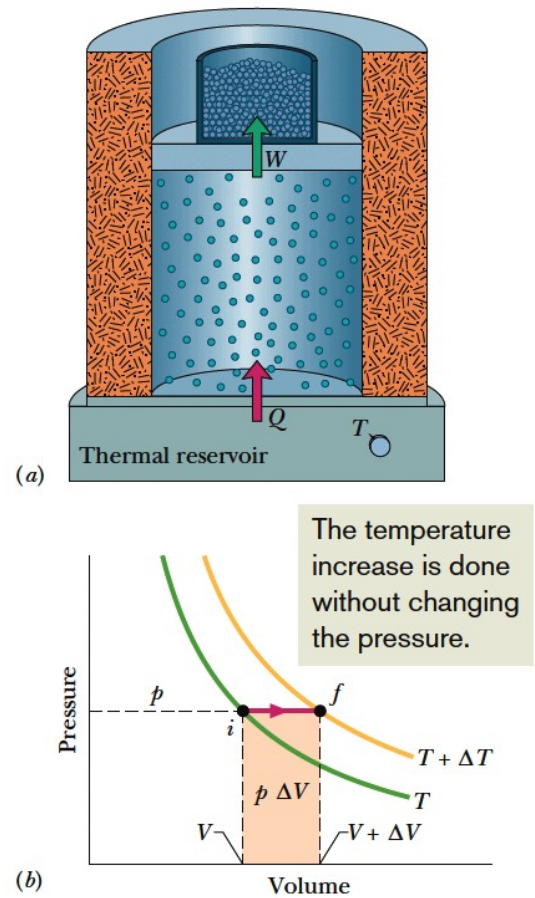

Figure 19-11 (*a*) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-pressure process. Heat is added and work is done in lifting the loaded piston. (*b*) The process on a p-V diagram. The work $p\,\Delta V$ is given by the shaded area.

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19-8 Degree of Freedom and Molar Specific Heats

Learning Objectives

19.39 Identify that a degree of freedom is associated with each way a gas can store energy (translation, rotation, and oscillation).

19.40 Identify that an energy of ½ kT per molecule is associated with each degree of freedom.

19.41 Identify that a monatomic gas can have an internal energy consisting of only translational motion.

19.42 Identify that at low temperatures a diatomic gas has energy in only translational motion, at higher temperatures it also has energy in molecular rotation, and at even higher temperatures it can also have energy in molecular oscillations.

19.43 Calculate the molar specific heat for monatomic and diatomic ideal gases in a constant-volume process and a constant-pressure process.

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19-8 Degree of Freedom and Molar Specific Heats

Equipartition of Energy

Table 19-3 Degrees of Freedom for Various Molecules

Molecule	Example	Degrees of Freedom: Translational	Rotational	Total (f)	Predicted Molar Specific Heats: C_V (Eq. 19-51)	$C_p = C_V + R$
Monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	CH_4	3	3	6	$3R$	$4R$

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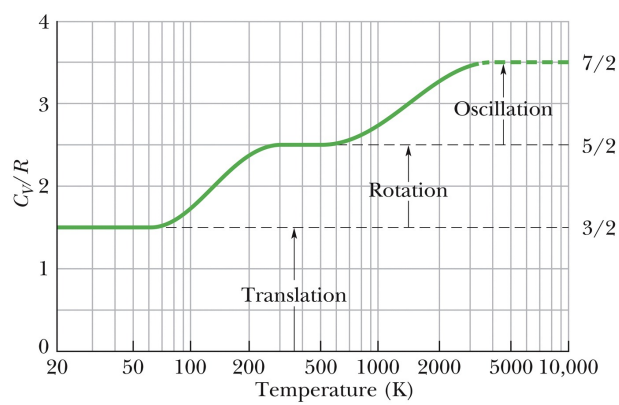
Every kind of molecule has a certain number f of *degrees of freedom*, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it—on average—an energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole).

C_V/R versus temperature for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.



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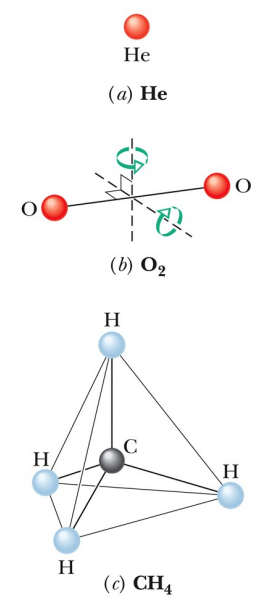

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Models of molecule as used in kinetic theory

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