

Kinetic Theory

Reading: Chapter 19

Ideal Gases

Ideal gas law:

$$pV = nRT,$$

where

p = pressure

V = volume

n = number of moles of gas

$R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$ is the **gas constant**.

T = absolute temperature

All gases behave like ideal gases at low enough densities.

Work Done by an Ideal Gas at Constant Temperature

Isothermal expansion: During the expansion, the temperature is kept constant.

Isothermal compression: During the compression, the temperature is kept constant.

Using the ideal gas law, an *isotherm* on a p - V diagram is given by

$$p = \frac{nRT}{V}.$$

Work done by an ideal gas during an isothermal expansion from V_i to V_f :

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

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} dV.$$

Since T is constant in an isothermal expansion,

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT [\ln V]_{V_i}^{V_f}.$$

Since $\ln a - \ln b = \ln (a/b)$,

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

For isothermal expansion, $V_f > V_i$, W is positive.

For isothermal compression, $V_f < V_i$, W is negative.

Other thermodynamic processes:

For constant-volume processes, $W = 0$.

For constant-pressure processes, $W = p(V_f - V_i) = p\Delta V$.

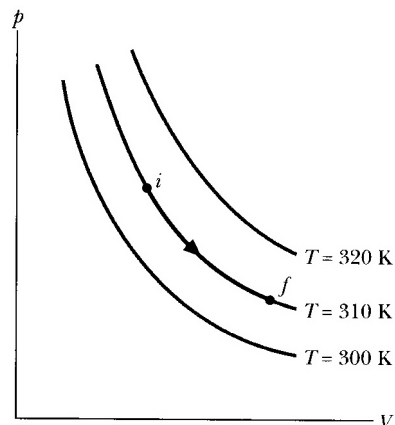


FIG. 19-2 Three isotherms on a p - V diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state i to a final state f . The path from f to i along the isotherm would represent the reverse process—that is, an isothermal compression.

Examples

19-1 A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

Since $pV = nRT$,

$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f} = nR.$$

$$p_f = p_i \frac{V_i}{V_f} \frac{T_f}{T_i}$$

$$= 15 \text{ atm} \left(\frac{12}{8.5} \right) \left(\frac{273 + 35}{273 + 20} \right)$$

$$= 22.3 \text{ atm (ans)}$$

19-2 One mole of oxygen (assume it to be an ideal gas) expands at a constant temperature T of 310 K from an initial volume V_i of 12 L to a final volume V_f of 19 L.

(a) How much work is done by the expanding gas?

(b) How much work is done by the gas during an isothermal compression from $V_i = 19$ L to $V_f = 12$ L?

$$\begin{aligned} \text{(a)} \quad W &= nRT \ln \frac{V_f}{V_i} \\ &= (1)(8.31)(310) \ln \frac{19}{12} \\ &= 1184 \text{ J (ans)} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad W &= nRT \ln \frac{V_i}{V_f} \\ &= (1)(8.31)(310) \ln \frac{12}{19} \\ &= -1184 \text{ J (ans)} \end{aligned}$$

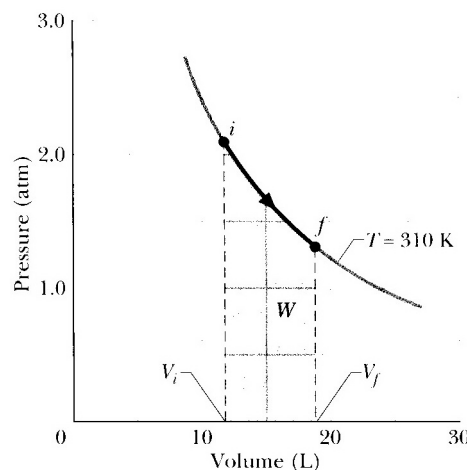


FIG. 19-3 The shaded area represents the work done by 1 mol of oxygen in expanding from V_i to V_f at a constant temperature T of 310 K.

Work is done on the gas to compress it.

Pressure, Temperature and RMS Speed

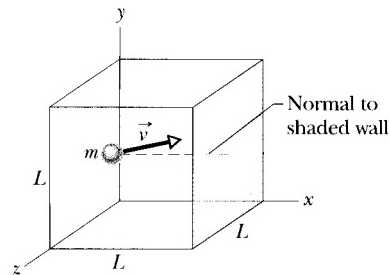


FIG. 19-4 A cubical box of edge length L , containing n moles of an ideal gas. A molecule of mass m and velocity \vec{v} is about to collide with the shaded wall of area L^2 . A normal to that wall is shown.

Consider n moles of an ideal gas in a cubical box of volume V at temperature T .

The gas molecules are moving in the box.

When they collide with the walls, the collision is elastic and momentum is transferred to the walls.

Using Newton's second law, this change in momentum results in a force acting on the wall.

This force contributes to the pressure of the gas.

In the x direction, the velocity of a molecule of mass m changes from v_x to $-v_x$ when it collides with the shaded wall.

Change in momentum $\Delta p_x = 2mv_x$.

The time between collisions $\Delta t = 2L/v_x$.

Hence the rate at which momentum is transferred to the shaded wall is:

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

Using Newton's law, this is the force exerted by the gas on the shaded wall. Summing up the forces due to all gas molecules,

$$F = \frac{mv_{1x}^2 + \cdots + mv_{Nx}^2}{L} = \frac{m}{L} (v_{1x}^2 + \cdots + v_{Nx}^2).$$

Pressure:

$$p = \frac{F}{L^2} = \frac{m}{L^3} (v_{1x}^2 + \cdots + v_{Nx}^2).$$

To simplify this expression, let

$$\langle v_x^2 \rangle = \frac{1}{N} (v_{1x}^2 + \cdots + v_{Nx}^2).$$

Also, $L^3 = V$. Therefore,

$$p = \frac{mN \langle v_x^2 \rangle}{V}.$$

Since mN is the total mass of the gas, $mN = nM$, where
 n = number of moles of gas,
 M = mass of 1 mole of gas (the molar mass of the gas).

$$p = \frac{nM \langle v_x^2 \rangle}{V}.$$

Since $v^2 = v_x^2 + v_y^2 + v_z^2$, and $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, we have

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle.$$

Hence

$$p = \frac{nM \langle v^2 \rangle}{3V}.$$

The **root-mean-square speed** v_{rms} for N molecules is defined by

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{1}{N} (v_1^2 + \cdots + v_N^2)}.$$

This yields

$$p = \frac{nM v_{\text{rms}}^2}{3V}.$$

This tells us that the (macroscopic) pressure of the gas depends on the (microscopic) speed of the molecules.

Using the ideal gas law, $pV = nRT$, we have

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

Example 19-3 Here are five numbers: 5, 11, 32, 67, 89.

- (a) What is the average value $\langle n \rangle$ of these numbers?
 (b) What is the rms value n_{rms} of these numbers?

$$(a) \quad \langle n \rangle = \frac{5 + 11 + 32 + 67 + 89}{5} = 40.8 \quad (\text{ans})$$

$$(b) \quad n_{\text{rms}} = \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + 89^2}{5}} = 52.1 \quad (\text{ans})$$

Translational Kinetic Energy

The translational kinetic energy of the gas:

$$\langle K \rangle = \left\langle \frac{1}{2} mv^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} mv_{\text{rms}}^2.$$

Since $v_{\text{rms}} = \sqrt{3RT/M}$,

$$\langle K \rangle = \left(\frac{1}{2} m \right) \frac{3RT}{M}.$$

Since $M = N_A m$, where N_A is the Avogadro's number (number of molecules in 1 mole = $6.02 \times 10^{23} \text{ mol}^{-1}$),

$$\langle K \rangle = \frac{3RT}{2N_A}.$$

This is generally written as

$$\boxed{\langle K \rangle = \frac{3}{2} kT},$$

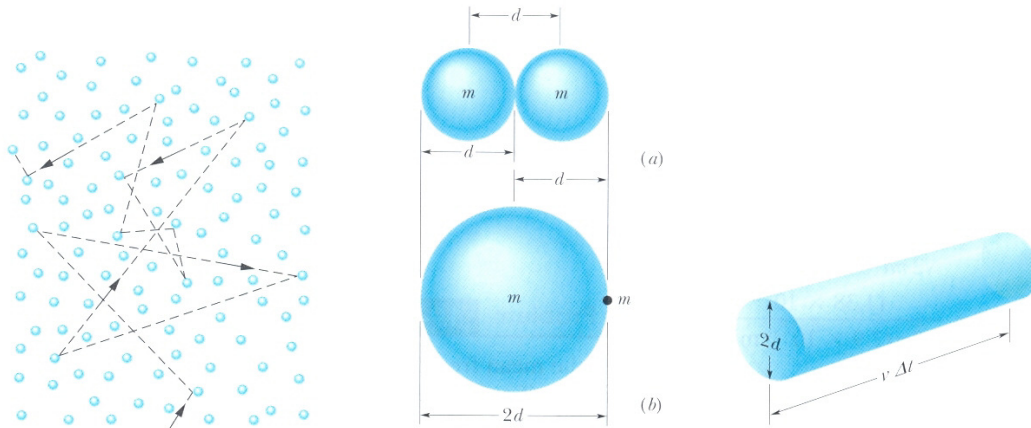
where k is called the **Boltzmann constant**, given by

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J mol}^{-1} \text{ K}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

Conclusion:

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.

Mean Free Path



Mean free path λ is the average distance traversed by a molecule between collisions.

A collision will take place if the centers of two molecules come within a distance d of each other.

Consider a single molecule traveling at constant speed v and assume that all other molecules are at rest.

In time Δt , the center of the moving molecule sweeps out a cylinder of length $v\Delta t$ and radius d ; any other molecule whose center lies in this cylinder will be collided.

Volume of the cylinder = $(\pi d^2)(v\Delta t)$.

Number of molecules in the cylinder = $(\pi d^2)(v\Delta t)(N/V)$.

Mean free path:

$$\lambda = \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} = \frac{v\Delta t}{\pi d^2 v\Delta t N/V} = \frac{1}{\pi d^2 N/V}$$

However, since all molecules are moving, the expression should include an extra factor of $1/\sqrt{2}$. That is,

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$$

To obtain the extra factor, let \mathbf{v}_1 and \mathbf{v}_2 be velocity of two molecules. Then the relative velocity is estimated as

$$\mathbf{v}_{rel}^2 = (\mathbf{v}_1 - \mathbf{v}_2) \cdot (\mathbf{v}_1 - \mathbf{v}_2) = v_1^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2 + v_2^2.$$

Averaging both sides, and noting that $\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = 0$,

$$\langle \mathbf{v}_{rel}^2 \rangle = \langle v_1^2 \rangle - 2\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle + \langle v_2^2 \rangle = 2\langle v^2 \rangle.$$

It becomes reasonable to estimate that

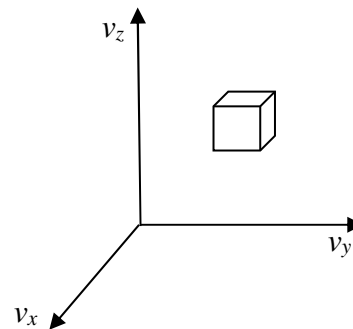
$$\langle \mathbf{v}_{rel} \rangle = \sqrt{2}\langle v \rangle.$$

Maxwell Distribution of Molecular Speeds

Maxwell found that when the probability of finding a molecule at an energy state E is

$$P(E) \propto \exp\left(-\frac{E}{k_B T}\right).$$

In the state space, the probability of finding a molecule in a cube of sides dv_x , dv_y , dv_z at velocity (v_x, v_y, v_z) is



$$\begin{aligned} & P(v_x, v_y, v_z) dv_x dv_y dv_z \\ &= A \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z \\ &= A \exp\left(-\frac{mv^2}{2k_B T}\right) dv_x dv_y dv_z. \end{aligned}$$

In spherical coordinates, the volume with velocity between v and $v + dv$ is $4\pi v^2 dv$. Hence the probability of finding a molecule with velocity between v and $v + dv$ is

$$P(v)dv = A \exp\left(-\frac{mv^2}{2k_B T}\right) 4\pi v^2 dv.$$

A is a constant satisfying

$$\int_0^{\infty} P(v)dv = 1.$$

The mathematical result is $A = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$. Final result:

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right).$$

Fraction of molecules with speed between v_1 and v_2

$$\text{frac} = \int_{v_1}^{v_2} P(v)dv.$$

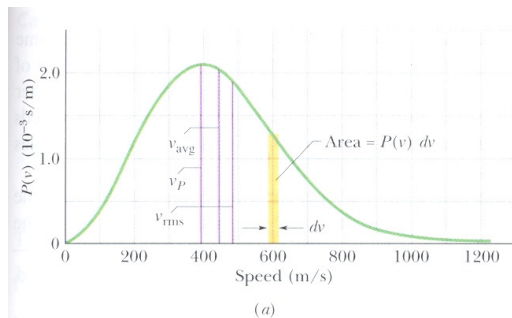
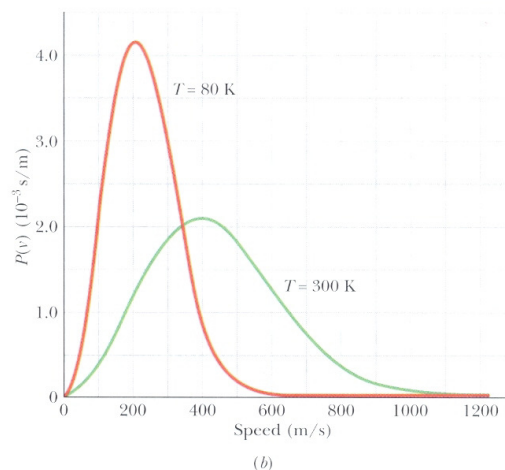


FIG. 19-8 (a) The Maxwell speed distribution for oxygen molecules at $T = 300$ K. The three characteristic speeds are marked. (b) The curves for 300 K and 80 K. Note that the molecules move more slowly at the lower temperature. Because these are probability distributions, the area under each curve has a numerical value of unity.



Average speed

$$\langle v \rangle = \int_0^{\infty} vP(v)dv = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}.$$

Mean square speed

$$\langle v^2 \rangle = \int_0^{\infty} v^2 P(v) dv = \frac{3k_B T}{m}.$$

rms speed

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

Most probable speed

$$v_P = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}.$$

Internal Energy

Consider a monatomic ideal gas (e.g. helium, neon, argon)

Internal energy:

translational kinetic energy of the atoms

no rotational kinetic energy (because monatomic)

no potential energy (because no intermolecular force)

For n moles of the gas,

number of molecules = nN_A

average kinetic energy of a molecule = $\frac{3}{2}kT$

total internal energy:

$$E_{\text{int}} = (nN_A) \left(\frac{3}{2} kT \right).$$

Since $N_A k = R$,

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

The internal energy E_{int} of an ideal gas is a function of the gas temperature only; it does not depend on its pressure or density.

Molar Specific Heat at Constant Volume

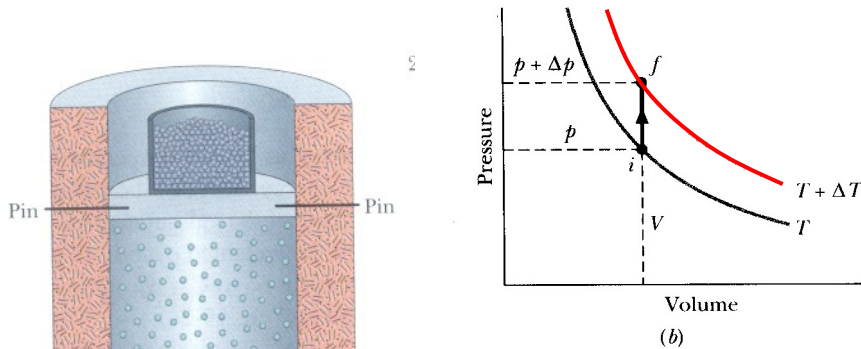


FIG. 19-9 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-volume process. Heat is added, but no work is done. (b) The process on a p - V diagram.

Using the first law of thermodynamics,

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

Since the volume is fixed, $W = 0$. Furthermore,

$$\Delta E_{\text{int}} = \frac{3}{2} nR\Delta T.$$

Therefore,

$$\frac{3}{2} nR\Delta T = Q.$$

Molar specific heat at constant volume:

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

$$C_V = \frac{3}{2} R \quad (\text{monatomic gas}).$$

Its value is $C_V = 12.5 \text{ Jmol}^{-1}\text{K}^{-1}$.

General Kinds of Gases

Polyatomic molecules possess both translational and rotational kinetic energy.

Hence their internal energy and specific heat are greater than those of monatomic gases. In general, if the molar specific heat at constant volume is C_V , then

$$E_{\text{int}} = nC_V T,$$

and

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

A change in the internal energy E_{int} of an ideal gas at constant volume depends on the change in the gas temperature only; it does not depend on what type of process produces the change in temperature.

path 1: constant volume

path 2: constant pressure

path 3: adiabatic compression

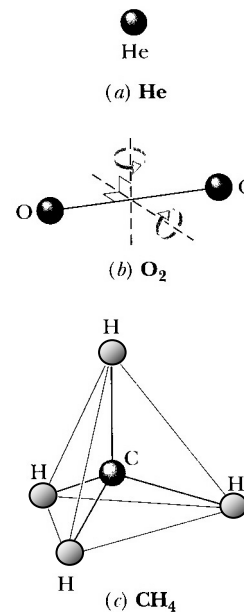


FIG. 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.

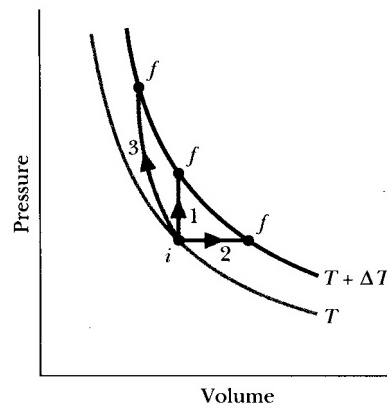


FIG. 19-10 Three paths representing three different processes that take an ideal gas from an initial state i at temperature T to some final state f at temperature $T + \Delta T$. The change ΔE_{int} in the internal energy of the gas is the same for these three processes and for any others that result in the same change of temperature.

Molar Specific Heat at Constant Pressure

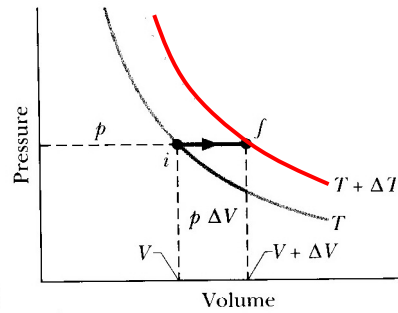
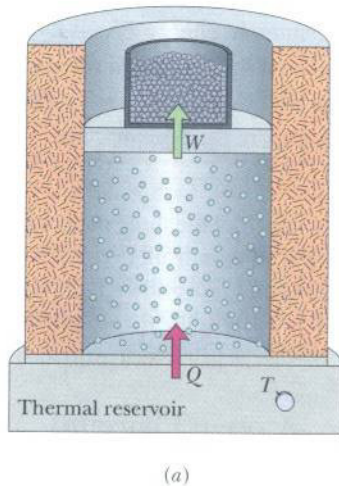


FIG. 19-11 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-pressure process. Heat is added and work is done in lifting the loaded piston. (b) The process on a p - V diagram. The work $p \Delta V$ is given by the shaded area.

Using the first law of thermodynamics,

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

For ideal gases, $pV = nRT$. Thus for work done at constant pressure,

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

Furthermore,

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

Therefore,

$$nC_V \Delta T = Q - nR\Delta T, \Rightarrow Q = nC_V \Delta T + nR\Delta T.$$

Molar specific heat at constant pressure:

$$C_P = \frac{Q}{n\Delta T}, \Rightarrow \boxed{C_P = C_V + R.}$$

Equipartition of Energy (Maxwell)

If a kind of molecule has f independent ways to store energy, then it has f degrees of freedom. Each degree of freedom has an average energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole) associated with it.

e.g. helium: 3 translational + 0 rotational

$$\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T, \text{ and } C_V = \frac{3}{2}R.$$

e.g. oxygen: 3 translational + 2 rotational

$$\Delta E_{\text{int}} = \frac{5}{2}nR\Delta T, \text{ and } C_V = \frac{5}{2}R.$$

e.g. methane: 3 translational + 3 rotational

$$\Delta E_{\text{int}} = 3nR\Delta T, \text{ and } C_V = 3R.$$

In general,

$$\Delta E_{\text{int}} = \frac{f}{2}nR\Delta T, \text{ and } C_V = \frac{f}{2}R.$$

TABLE 19-3

Degrees of Freedom for Various Molecules

Molecule	Example	Degrees of Freedom			Predicted Molar Specific Heats	
		Translational	Rotational	Total (f)	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	$3R$	$4R$

TABLE 19-2

Molar Specific Heats at Constant Volume

Molecule	Example	C_V (J/mol·K)
Monatomic	Ideal	$\frac{3}{2}R = 12.5$
	Real	He 12.5
		Ar 12.6
Diatomic	Ideal	$\frac{5}{2}R = 20.8$
	Real	N ₂ 20.7
		O ₂ 20.8
Polyatomic	Ideal	$3R = 24.9$
	Real	NH ₄ 29.0
		CO ₂ 29.7

Example

19-7 A bubble of 5 mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT of 20°C at constant pressure. As a result, the bubble expands.

(a) How much energy is added to the helium as heat during the increase and expansion?

(b) What is the change ΔE_{int} in the internal energy of the helium during the temperature increase?

(c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

$$(a) \quad C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$Q = nC_P\Delta T = n\left(\frac{5}{2}R\right)C_V\Delta T$$

$$= (5)(2.5)(8.31)(20)$$

$$= 2080 \text{ J (ans)}$$

$$(b) \quad \Delta E_{\text{int}} = nC_V\Delta T = n\left(\frac{3}{2}R\right)C_V\Delta T$$

$$= (5)(1.5)(8.31)(20)$$

$$= 1250 \text{ J (ans)}$$

(c) Using the first law of thermodynamics,

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

$$= 2077.5 - 1246.5$$

$$= 831 \text{ J (ans)}$$

19-8 We transfer 1000 J to a diatomic gas, allowing it to expand with the pressure held constant. The gas molecules rotate but do not oscillate. How much of the 1000 J goes into the increase of the gas's internal energy? Of that amount, how much goes into ΔK_{tran} (the kinetic energy of the translational motion of the molecules) and ΔK_{rot} (the kinetic energy of their rotational motion)?

$$Q = 1000 \text{ J}$$

A diatomic gas has 5 degrees of freedom.

Therefore, $C_V = 5R/2$ and $C_P = 7R/2$.

At constant pressure,

$$\Delta T = \frac{Q}{7nR/2}$$

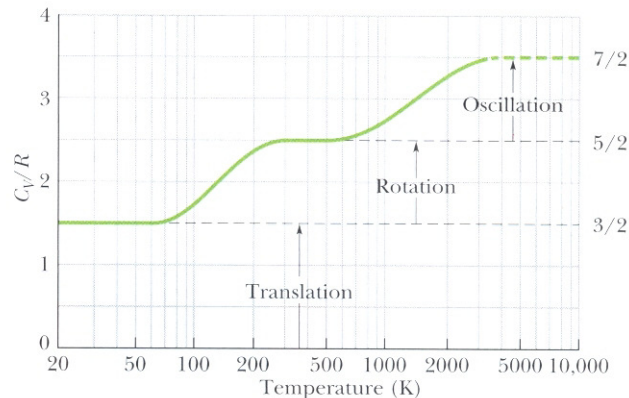
$$\begin{aligned}\Delta E_{\text{int}} &= nC_V \Delta T = n \left(\frac{5}{2} R \right) \frac{Q}{7nR/2} = \frac{5}{7} Q \\ &= \left(\frac{5}{7} \right) 1000 = 714.3 \text{ J} \quad (\text{ans})\end{aligned}$$

There are 3 translational degrees of freedom and 2 rotational degrees of freedom. Thus,

$$\begin{aligned}\Delta K_{\text{tran}} &= n \left(\frac{3}{2} R \right) \Delta T = n \left(\frac{3}{2} R \right) \frac{Q}{7nR/2} = \frac{3}{7} Q \\ &= \left(\frac{3}{7} \right) 1000 = 428.6 \text{ J} \quad (\text{ans})\end{aligned}$$

$$\begin{aligned}\Delta K_{\text{rot}} &= n \left(\frac{2}{2} R \right) \Delta T = nR \frac{Q}{7nR/2} = \frac{2}{7} Q \\ &= \left(\frac{2}{7} \right) 1000 = 285.7 \text{ J} \quad (\text{ans})\end{aligned}$$

A Hint of Quantum Theory



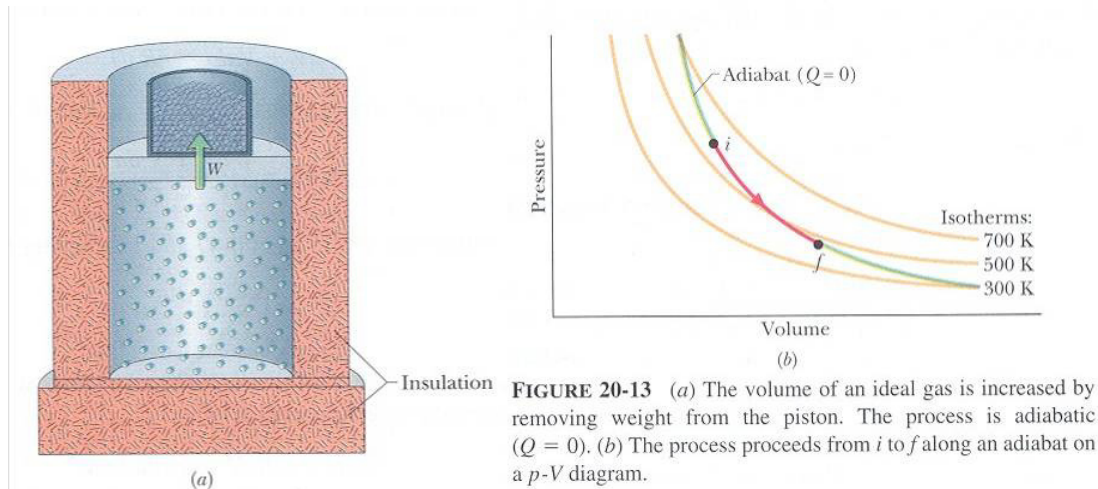
Below about 80 K, $C_V/R = 1.5 \Rightarrow 3$ translational degrees of freedom.

As the temperature increases, C_V/R increases to 2.5, two additional degrees of freedom. These are the rotational degrees of freedom, and this motion requires a certain minimum amount of energy.

In quantum theory, an *energy quantum* is required to excite the rotation. This energy is not available at low temperatures.

Above 1000 K, C_V/R increases to 3.5, because the oscillatory degrees of freedom are excited. The energy quantum required to excite oscillations is not available at lower temperatures.

The Adiabatic Expansion of an Ideal Gas



For adiabatic processes, $Q = 0$.

Using the first law of thermodynamics, adiabatic compression causes heating, adiabatic expansion causes cooling.

We can prove:

$$pV^\gamma = \text{constant},$$

where $\gamma = C_p/C_v$, the ratio of the molar specific heats. Or,

$$p_1V_1^\gamma = p_2V_2^\gamma.$$

Using the ideal gas equation, $pV = nRT$,

$$\left(\frac{nRT}{V}\right)V^\gamma = \text{constant},$$

$$TV^{\gamma-1} = \text{constant}.$$

or

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}.$$

Example: Fog formation when a cold can of soft drink is opened.

Proof:

First law of thermodynamics for a small expansion:

$$dE_{\text{int}} = dQ - dW,$$

where

$$dE_{\text{int}} = nC_V dT,$$

$$dQ = 0 \text{ for adiabatic processes,}$$

$$dW = p dV.$$

From the ideal gas equation, $pV = nRT$, so that

$$dW = \frac{nRT}{V} dV.$$

Substituting,

$$nC_V dT = 0 - \frac{nRT}{V} dV,$$

we arrive at the differential equation

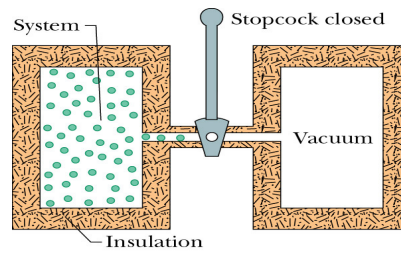
$$\frac{dV}{dT} = -\left(\frac{C_V}{R}\right) \frac{V}{T}.$$

Solution (verify by substitution):

$$V = \text{constant} \cdot T^{-C_V/R}, \quad \Rightarrow \quad TV^{R/C_V} = \text{constant}.$$

Since $R/C_V = (C_P - C_V)/C_V = \gamma - 1$, we get the adiabatic laws.

Free Expansion



No work is done: $W = 0$

No heat is transferred: $Q = 0$

Hence no change in internal energy: $\Delta E_{\text{int}} = Q - W = 0$.

For ideal gases, this implies no change in temperature:

$$T_i = T_f \quad \text{or} \quad p_i V_i = p_f V_f$$

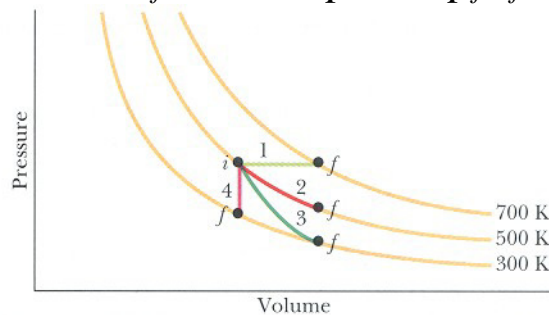


FIGURE 20-14 A p - V diagram representing four special processes for an ideal gas. See Table 20-5.

TABLE 20-5 FOUR SPECIAL PROCESSES

PATH IN FIG. 20-14	CONSTANT QUANTITY	PROCESS TYPE	SOME SPECIAL RESULTS
			($\Delta E_{\text{int}} = Q - W$ and $\Delta E_{\text{int}} = nC_V \Delta T$ for all paths)
1	p	Isobaric	$Q = nC_p \Delta T$; $W = p\Delta V$
2	T	Isothermal	$Q = W = nRT \ln(V_f/V_i)$; $\Delta E_{\text{int}} = 0$
3	pV^γ , $TV^{\gamma-1}$	Adiabatic	$Q = 0$; $W = -\Delta E_{\text{int}}$
4	V	Isochoric	$Q = \Delta E_{\text{int}} = nC_V \Delta T$; $W = 0$

Example

19-10 1 mol of oxygen expands adiabatically from an initial volume of 12 L at 310 K to a final volume of 19 L.

(a) What would be the final temperature of the gas? Oxygen is diatomic and here has rotation but not oscillation.

(b) What is the initial and final pressure of the gas?

(c) If, instead, the gas had expanded freely from the initial volume to the final volume, what would be the final temperature and pressure?

(a) Oxygen has 5 degrees of freedom, therefore

$$C_V = \frac{5}{2}R, \quad C_P = \frac{7}{2}R, \quad \gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1.4$$

Since $TV^{\gamma-1} = \text{constant}$,

$$T_f = T_i \frac{V_i^{\gamma-1}}{V_f^{\gamma-1}} = 310 \left(\frac{12}{19} \right)^{1.4-1} = 258 \text{ K} \quad (\text{ans})$$

(b) Using ideal gas law, initial pressure:

$$p_i = \frac{nRT_i}{V_i} = \frac{(1)(8.31)(310)}{12 \times 10^{-3}} = 214675 \text{ Nm}^{-2} \approx 2.12 \text{ atm}$$

Final pressure:

$$p_f = \frac{nRT_f}{V_f} = \frac{1 \times 8.31 \times 258}{19 \times 10^{-3}} = 112841 \text{ Nm}^{-2} \approx 1.11 \text{ atm}$$

(c) For free expansion, $T_i = T_f$ and $p_i V_i = p_f V_f$

final temperature = 310 K

final pressure

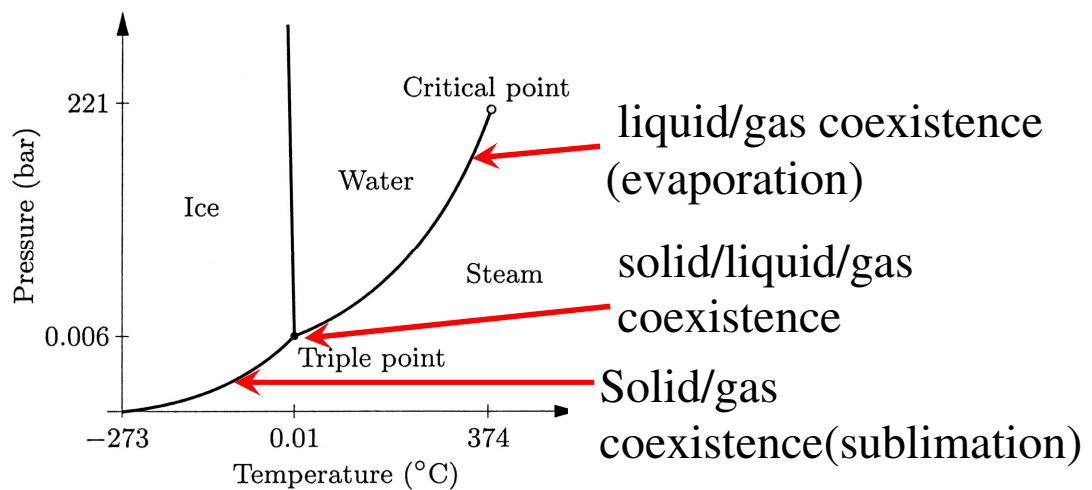
$$= p_f = p_i \frac{V_i}{V_f} = 214675 \left(\frac{12}{19} \right) = 135584 \text{ Nm}^{-2} \approx 1.34 \text{ atm}$$

(ans)

Phase Transitions

A phase transition is a “discontinuous” change in the properties of a substance when its environment changes infinitesimally. For example water can change from solid to liquid at 0 °C or from liquid to gas at 100 °C. But other factors, such as pressure, can also affect a phase transition besides temperature.

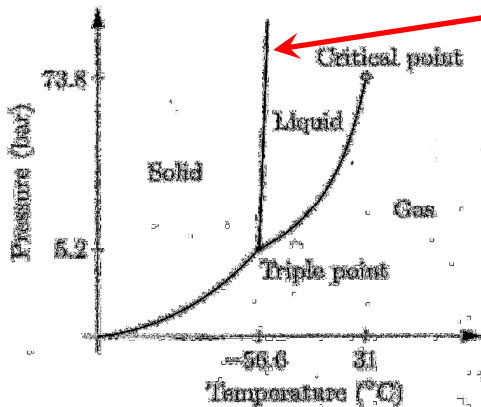
The phase diagram show the phases (solid, liquid, gas) as a function of T and P



- The lines in the phase diagram indicate the conditions that two phases can coexist in equilibrium. (See “dry ice bomb” in YouTube.)
- In the regions separated by the phase lines, respectively, ice, water and steam are the most stable phases.
- However, “metastable” phases can still exist.
- Example: “supercooled” water can exist at the left of the solid/liquid coexistence line.
- Example: “Superheated” water can exist at the right of the liquid/gas coexistence line.
- See “superheating” and “supercooling” in YouTube.

Compare the phase diagram for H_2O above to CO_2 below.

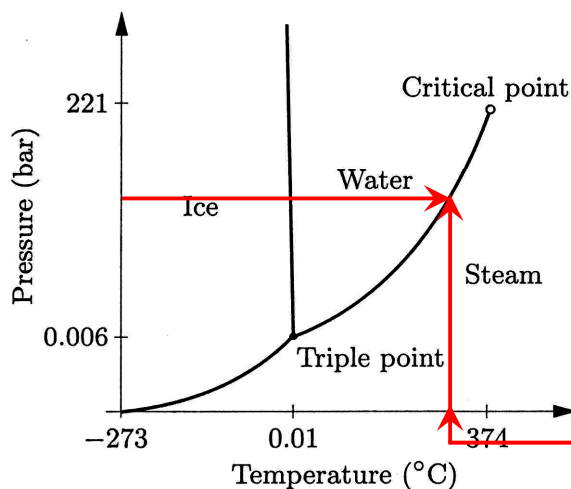
A very important difference is that the solid-liquid phase



boundary for CO_2 has a positive slope (melting temperature increases when pressure increase), which is the usual behavior. For H_2O , the solid-liquid boundary, actually has a negative slope (melting temperature decreases with increasing pressure), which is unusual. That is why we can skate on ice but not on any other solid surface!

At the phase boundary between liquid and gas, the liquid coexists at some temperature with gas at an appropriate pressure called the vapour pressure.

the vapor pressure



T ($^{\circ}C$)	P_v (bar)	L (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

The liquid-gas phase boundary has positive slope

- ⇒ ① At higher temperature, a greater pressure must be applied to keep the liquid and gas in coexistence
- ② At higher pressure, the gas becomes more dense
- ③ At the **critical point**, the liquid and dense gas becomes indistinguishable - then we call the system a **fluid**. (See “critical point of benzene” in YouTube.)

Vapor Pressure

The vapor pressure of a vapor is its pressure when it is in thermodynamic equilibrium with its condensed phase in a closed system.

All liquids have a tendency to evaporate, and some solids can sublime into a gaseous form.

Vice versa, all gases have a tendency to condense back to their liquid form, or deposit back to solid form.

The equilibrium vapor pressure is an indication of a liquid's evaporation rate. It relates to the tendency of particles to escape from the liquid (or a solid). A substance with a high vapor pressure at normal temperatures is often referred to as *volatile*.

Observations

1. The atmospheric pressure [boiling point](#) of a liquid (also known as the normal boiling point) is the temperature at which the vapor pressure equals the ambient atmospheric pressure. With any incremental increase in that temperature, the vapor pressure becomes sufficient to overcome atmospheric pressure and lift the liquid to form vapor bubbles inside the bulk of the substance.
2. [Bubble formation](#) deeper in the liquid requires a higher pressure, and therefore higher temperature, because the fluid pressure increases above the atmospheric pressure as the depth increases.
3. The boiling point of water [at high altitude](#) is lower than 100°C due to the lower atmospheric pressure.

4. When the temperature is lowered, the vapor pressure of water vapor decreases. Condensation of water takes place at the [dew point](#).

5. The [relative humidity](#) is the density of water vapor divided by saturated vapor density. It is also equal to the vapor pressure of water vapor divided by the saturated vapor pressure. When the relative humidity reaches 100%, condensation takes place.

6. The vapor pressure that a single component in a mixture contributes to the total pressure in the system is called [partial vapor pressure](#). For example, air at sea level, saturated with water vapor at 20 °C has a partial pressures of 23 mbar of water, and about 780 mbar of nitrogen, 210 mbar of oxygen and 9 mbar of argon.

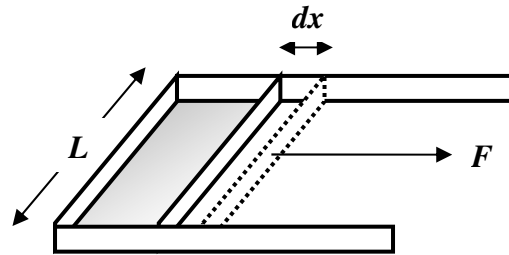
Surface Tension (Reference: Wikipedia)

Surface tension is a property of the surface of a [liquid](#) that allows it to resist an external force. It is revealed, for example, in floating of some objects on the surface of water, even though they are denser than water, and in the ability of some insects (e.g. [water striders](#)) and even reptiles ([basilisk](#)) to run on the water surface. This property is caused by [cohesion](#) of like molecules, and is responsible for many of the behaviors of liquids.

Surface tension has the [dimension](#) of [force](#) per unit [length](#), or of [energy](#) per unit [area](#). The two are equivalent—but when referring to energy per unit of area, people use the term [surface energy](#)—which is a more general term in the sense that it applies also to [solids](#) and not just liquids.

See Wikipedia for the examples and pictures.

Two Definitions



Let γ be the surface tension of the liquid interface.

Suppose the liquid interface is stretched by dx .

Applied force: $F = \gamma L$

Work done: $dW = Fdx = \gamma Ldx$

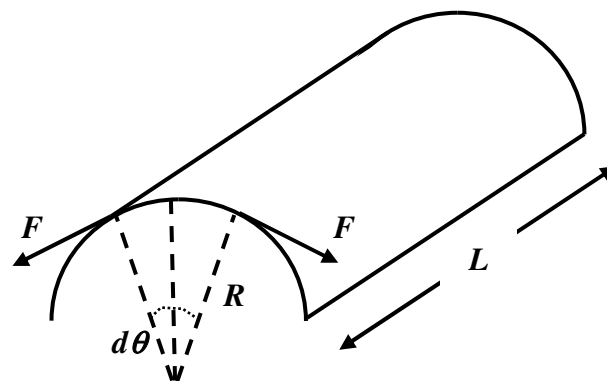
Increase in surface energy: $dE = dW = \gamma Ldx$

Surface energy per unit area: $\frac{dE}{Ldx} = \gamma$

This shows that the surface tension can be interpreted as the surface force per unit length, as well as the surface energy per unit area.

Remark: If the interface in the above experiment is a film, e.g. a soap film, then there is an interface above the film and interface below the film. The force, work done, and surface energy has to be multiplied by 2.

Surface Curvature and Pressure



Let Δp be the excess pressure inside the cylindrically curved interface.

Force on the curved segment due to the excess pressure
 $= \Delta p(LRd\theta)$

This is balanced by the vertical components of the surface tension

$$= 2\gamma L \sin\left(\frac{d\theta}{2}\right) \approx \gamma L d\theta$$

Equating the two forces, $\Delta p(LRd\theta) = \gamma L d\theta$

$$\Rightarrow \Delta p = \frac{\gamma}{R}$$

If the surface is curved in both the x and y directions,

$$\Delta p = \gamma \left(\frac{1}{R_x} + \frac{1}{R_y} \right)$$

Remark: This result is applicable to interfaces of a bulk droplet, e.g. a water drop. For interfaces of a film droplet, e.g. a soap bubble, the result should be multiplied by 2.

Capillary Action

Let r be the radius of the capillary tube.

Upward force due to surface tension $= (\gamma \cos \theta) 2\pi r$

Weight of the liquid column $= (\rho \pi r^2 h) g$

Equating the forces,

$$(\gamma \cos \theta) 2\pi r = (\rho \pi r^2 h) g \quad \Rightarrow$$

$$h = \frac{2\gamma \cos \theta}{\rho g r}$$

