

Kinetic Theory

Reading: Chapter 19 (except 19-6, 19-7, 19-10)

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, $W = p(V_f - V_i) = p\Delta V$.

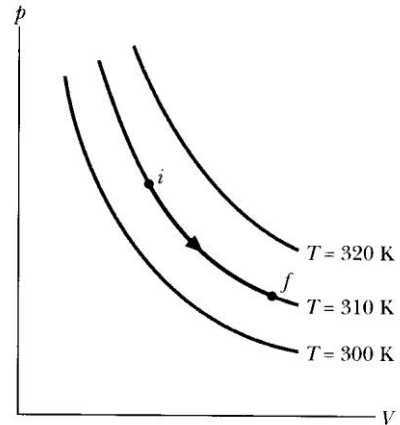


FIG. 19-2 Three isotherms on a p - V diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state i to a final state f . The path from f to i along the isotherm would represent the reverse process—that is, an isothermal compression.

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 $pV = nRT$,

$$\begin{aligned}\frac{p_i V_i}{T_i} &= \frac{p_f V_f}{T_f} = nR. \\ p_f &= p_i \frac{V_i}{V_f} \frac{T_f}{T_i} \\ &= 15 \text{ atm} \left(\frac{12}{8.5} \right) \left(\frac{273 + 35}{273 + 20} \right) \\ &= 22.3 \text{ atm (ans)}\end{aligned}$$

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?

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

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

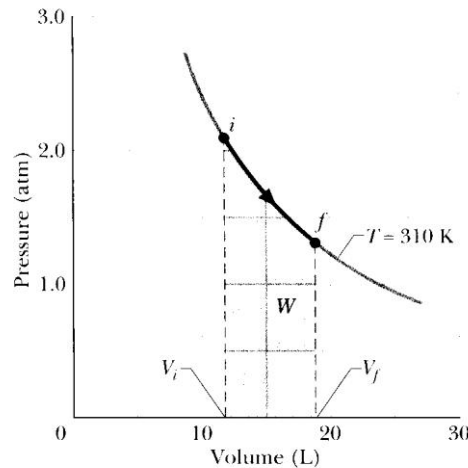


FIG. 19-3 The shaded area represents the work done by 1 mol of oxygen in expanding from V_i to V_f at a constant temperature T of 310 K.

Work is done on the gas to compress it.

Pressure, Temperature and RMS Speed

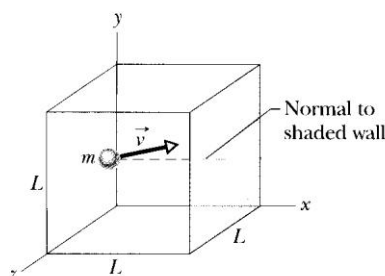


FIG. 19-4 A cubical box of edge length L , containing n moles of an ideal gas. A molecule of mass m and velocity \vec{v} is about to collide with the shaded wall of area L^2 . A normal to that wall is shown.

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,

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

Pressure:

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

To simplify this expression, let

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

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

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

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:

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

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.

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

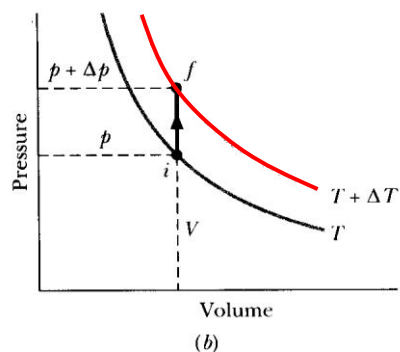
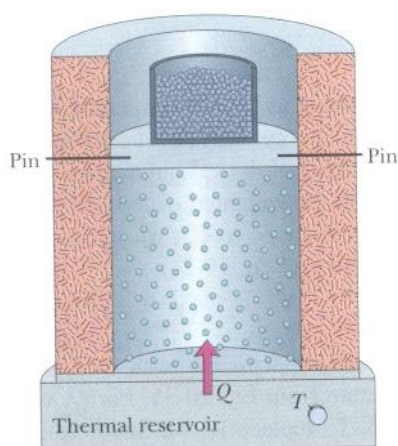


FIG. 19-9 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-volume process. Heat is added, but no work is done. (b) The process on a p - V diagram.

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

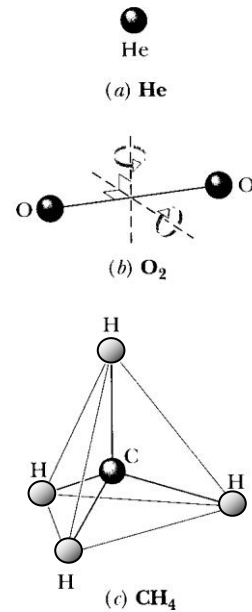


FIG. 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen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

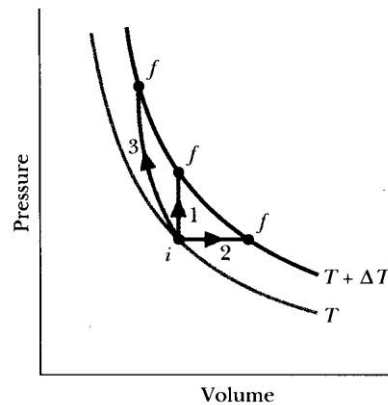
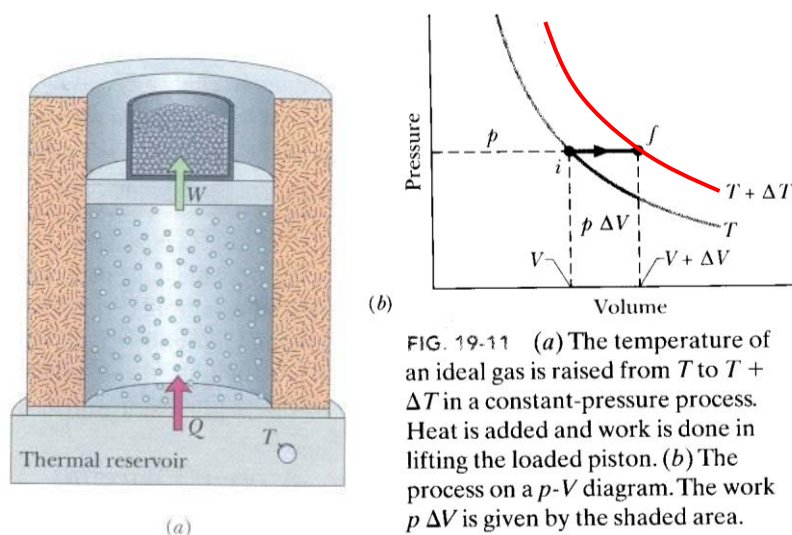


FIG. 19-10 Three paths representing three different processes that take an ideal gas from an initial state i at temperature T to some final state f at temperature $T + \Delta T$. The change ΔE_{int} in the internal energy of the gas is the same for these three processes and for any others that result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

Molar Specific Heat at Constant Pressure



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,

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

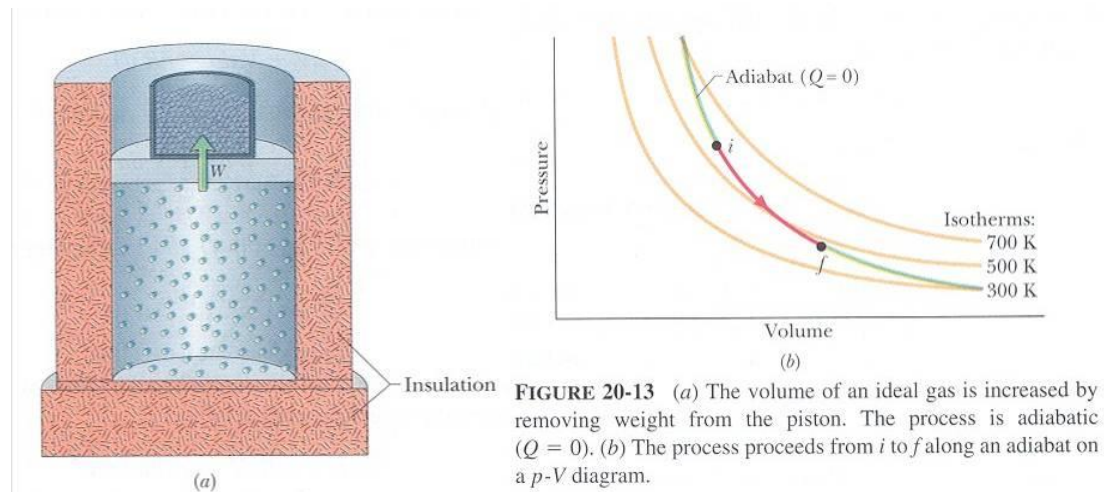
$$\begin{aligned}\Delta E_{\text{int}} &= nC_V\Delta T = n\left(\frac{5}{2}R\right)\frac{Q}{7nR/2} = \frac{5}{7}Q \\ &= \left(\frac{5}{7}\right)1000 = 714.3 \text{ J} \quad (\text{ans})\end{aligned}$$

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

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

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

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

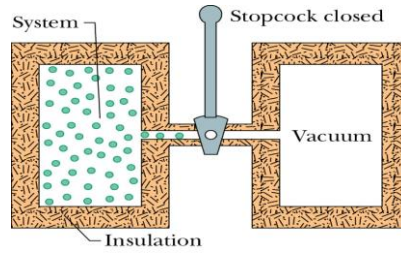
$$\frac{dV}{dT} = -\left(\frac{C_V}{R}\right)\frac{V}{T}.$$

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:

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

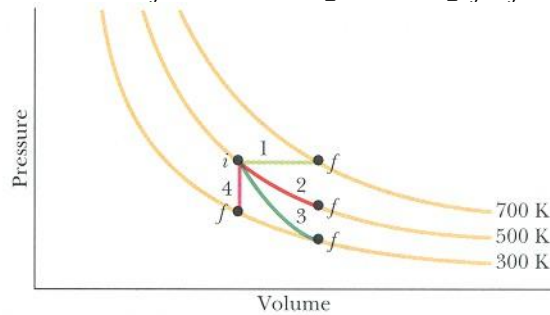


FIGURE 20-14 A p - V diagram representing four special processes for an ideal gas. See Table 20-5.

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?