

Chapter 19

The Kinetic Theory of Gases

1. The Kinetic Theory of Gases

The **kinetic theory of gases** relates the motion of atoms to the volume, pressure and temperature of gases.

2. Avogadro's Number

The mole is one of the seven SI base units. It is defined as follows:

“One mole is the number of atoms in a 12 g sample of carbon-12.”

The number of atoms or molecules in a mole is given (experimentally) by **Avogadro's number**:

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}.$$

The number of moles n contained in a sample of any substance is equal to the ratio of the number of molecules N in the sample to the number of molecules N_A in 1 mol:

$$n = \frac{N}{N_A}.$$

2. Avogadro's Number

The number of moles n is related to the mass of the sample M_{sam} and either the **molar mass** M (mass of 1 mole) or the molecular mass m (mass of one molecule) by:

$$n = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{mN_A},$$

where we used that $M = mN_A$.

3. Ideal Gases

Experimentally, it was found that the pressure p , volume V and temperature T for any gas are related by

$$pV = nRT,$$

where n is the number of moles of gas and R is the **gas constant** given by

$$R = 8.31 \text{ J/mol} \cdot \text{K}.$$

This is the **ideal gas law**. It holds for any gas at low density.

3. Ideal Gases

We can rewrite the ideal gas law in terms of the **Boltzmann constant** k , where

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

We can write nR as

$$nR = \frac{N}{N_A} (N_A k) = Nk.$$

The Ideal gas law can be written as

$$pV = NkT.$$

3. Ideal Gases

Work Done by an Ideal Gas at Constant Temperature

Consider an ideal gas in a piston-cylinder arrangement. Suppose that we allow the gas to expand from an initial volume V_i to a final volume V_f , while we keep the temperature T constant. Such a process is called an **isothermal expansion**. The reverse is an **isothermal compression**.

On a p - V diagram, an **isotherm** is a curve that connects points that have the same temperature. For n moles of an ideal gas, an isotherm is the graph of the equation

$$p = (nRT) \frac{1}{V} = (\text{constant}) \frac{1}{V}.$$

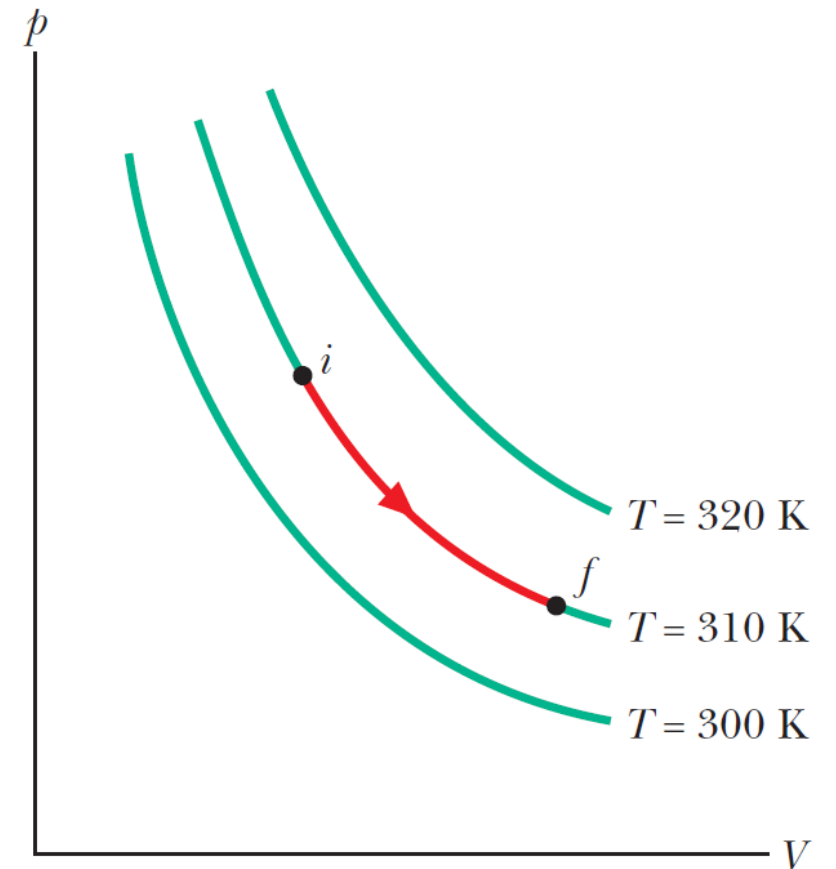
3. Ideal Gases

Work Done by an Ideal Gas at Constant Temperature

The figure shows three isotherms. An isothermal expansion (red curve) is shown too.

The work done by an ideal gas during an isothermal expansion is

$$\begin{aligned} W &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} \\ &= nRT [\ln V]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}. \end{aligned}$$



3. Ideal Gases



CHECKPOINT 1

An ideal gas has an initial pressure of 3 pressure units and an initial volume of 4 volume units. The table gives the final pressure and volume of the gas (in those same units) in five processes. Which processes start and end on the same isotherm?

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>p</i>	12	6	5	4	1
<i>V</i>	1	2	7	3	12

$$pV = nRT$$

$$T = \frac{pV}{nR}$$

a, b, d and e.

3. Ideal Gases

Example 2: A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

The ideal gas law for the initial and final states, respectively, reads

$$p_i V_i = nRT_i,$$

$$p_f V_f = nRT_f.$$

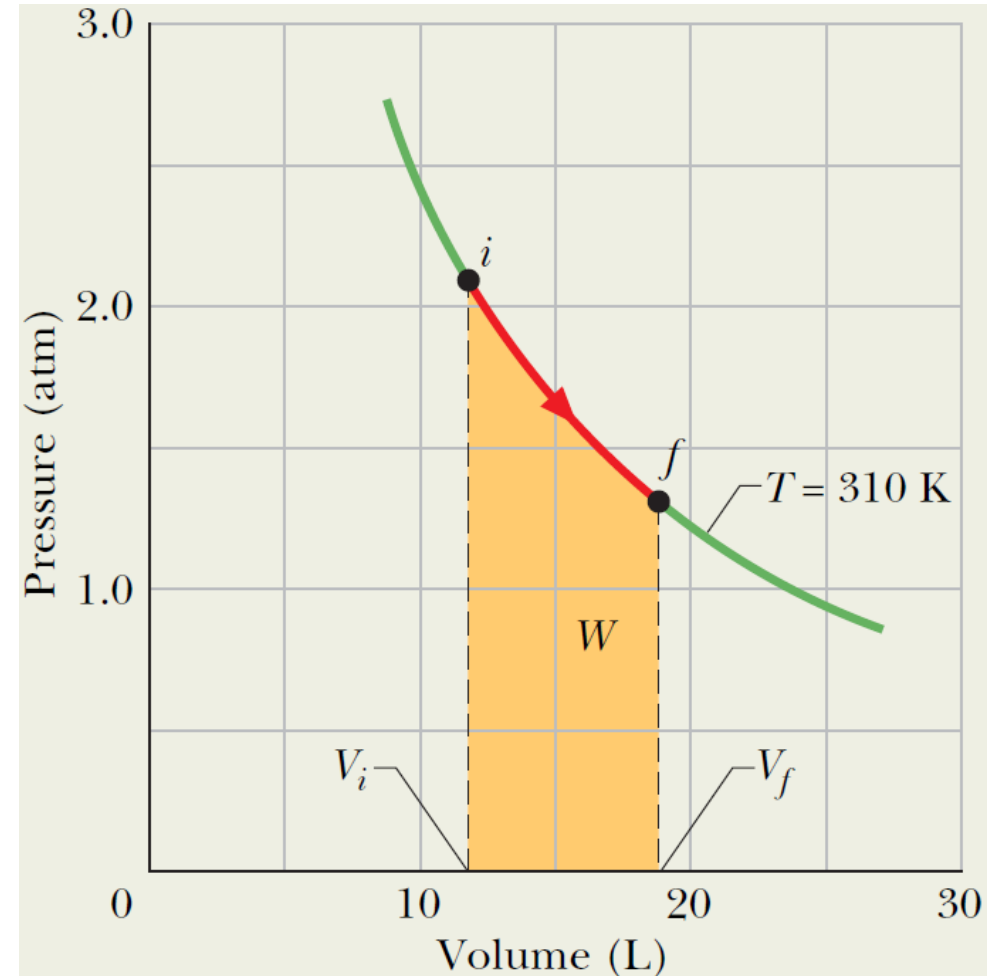
Dividing the second equation by the first and rearranging give

$$p_f = \frac{p_i V_i T_f}{V_f T_i} = \frac{(15 \text{ atm})(12 \text{ L})(308 \text{ K})}{(8.5 \text{ L})(293 \text{ K})} = 22 \text{ atm.}$$

3. Ideal Gases

Example 3: 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. How much work is done by the gas during the expansion?

$$\begin{aligned} W &= nRT \ln \frac{V_f}{V_i} \\ &= (1.00 \text{ mol}) \left(8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (310 \text{ K}) \ln \frac{19 \text{ L}}{12 \text{ L}} \\ &= 1180 \text{ J.} \end{aligned}$$



4. Pressure, Temperature, and RMS Speed

For a set of n values $\{x_1, x_2, \dots, x_n\}$, the **mean** value \bar{x} (or **average** value x_{avg}) is

$$\bar{x} = \frac{1}{n} (x_1 + x_2 + \dots + x_n).$$

The **root mean square** (rms) value x_{rms} is defined as

$$x_{\text{rms}} = \sqrt{\frac{1}{n} (x_1^2 + x_2^2 + \dots + x_n^2)}.$$

4. Pressure, Temperature, and RMS Speed

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

(a) What is the average value n_{avg} of these numbers?

$$n_{\text{avg}} = \frac{5 + 11 + 32 + 67 + 89}{5} = 40.8.$$

(b) What is the rms value n_{rms} of these numbers?

$$n_{\text{avg}} = \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + 89^2}{5}} = 51.1.$$

4. Pressure, Temperature, and RMS Speed

The pressure p exerted by n moles of an ideal gas is related to the rms speed v_{rms} of the molecules by

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

where M is the molar mass of the gas. Using the ideal gas law we write

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

Some RMS Speeds at Room Temperature ($T = 300 \text{ K}$)^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

5. Translational Kinetic Energy

The average translational kinetic energy of a single molecule of an ideal gas is

$$K_{\text{avg}} = \frac{1}{2} m v_{\text{rms}}^2 = \frac{1}{2} m \frac{3RT}{M} = \frac{3RT}{2N_A} = \frac{3}{2} kT. \quad \frac{M}{m} = N_A; R = kN_A$$

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.

5. Translational Kinetic Energy



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.

(a) All tie.

(b) 3,2 then 1.

$$K_{\text{avg}} = \frac{3}{2}kT$$

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

$$M = N_A m$$

5. Translational Kinetic Energy

Internal Energy E_{int}

We can assume that the internal energy E_{int} of a monatomic ideal gas is the sum of the translational kinetic energies of its atoms:

$$E_{\text{int}} = NK_{\text{avg}} = \frac{3}{2}NkT = \frac{3}{2}n(N_A k)T = \frac{3}{2}nRT.$$

“The internal energy of an ideal gas is a function of the gas temperature only.”

A temperature change of ΔT results in a change of internal energy ΔE_{int} given by

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

6. The Molar Specific Heats of an Ideal Gas

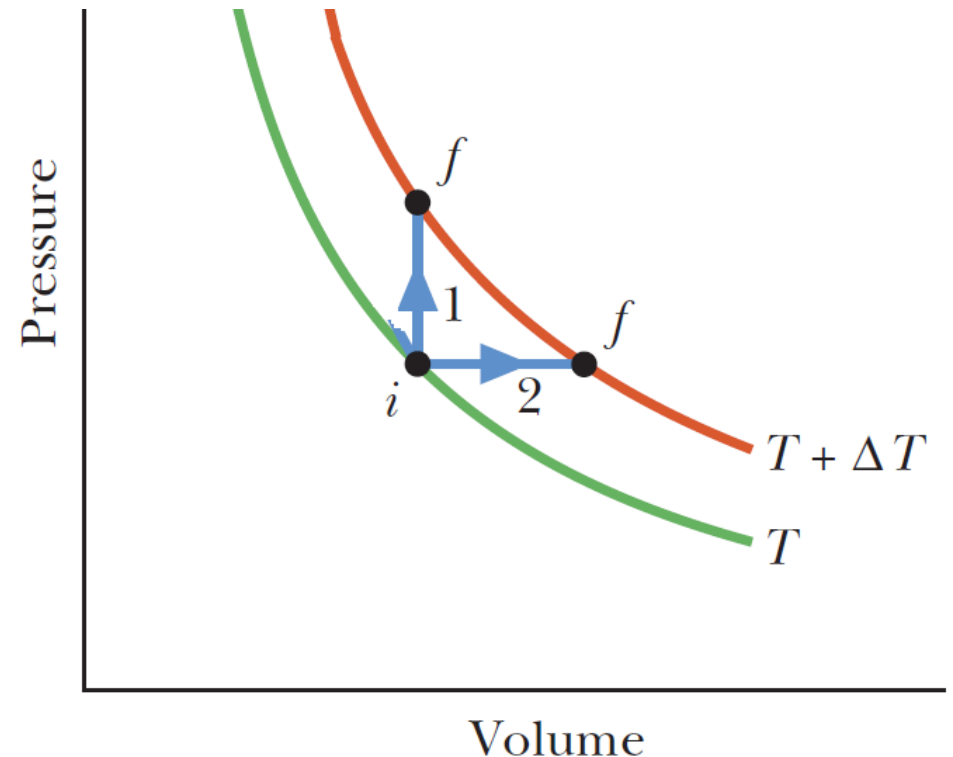
We can now use the expression for E_{int} to derive an expression for the molar specific heat of an ideal gas.

Remember that, for a solid or liquid

$$Q = C\Delta T = nc_{\text{mol}}\Delta T.$$

However, for gases, the heat Q depends on the details of a process. Thus, we shall derive two expressions for c_{mol} :

- (1) When the volume of the gas is kept constant.
- (2) When the pressure of the gas is kept constant.



6. The Molar Specific Heats of an Ideal Gas

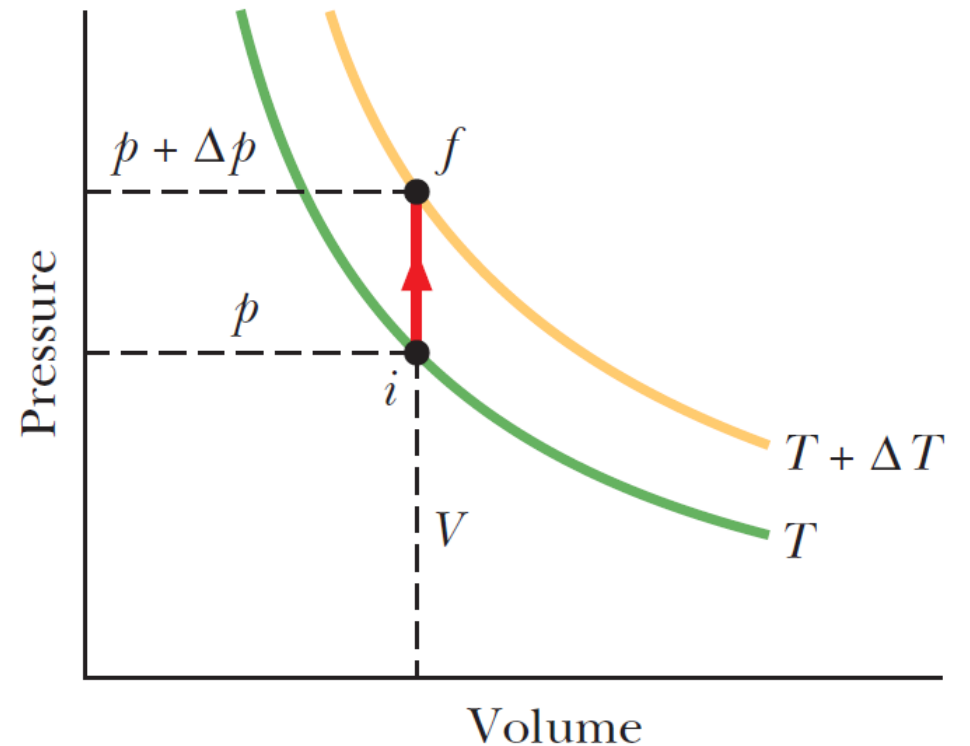
Molar Specific Heat at Constant Volume

In the process shown in the figure, the temperature of an ideal gas rises to $T + \Delta T$, and the pressure rises to $p + \Delta p$ while V is unchanged.

The heat Q added to the gas is related to ΔT by

$$Q = nC_V\Delta T$$

where C_V is the **molar specific heat at constant volume**.



6. The Molar Specific Heats of an Ideal Gas

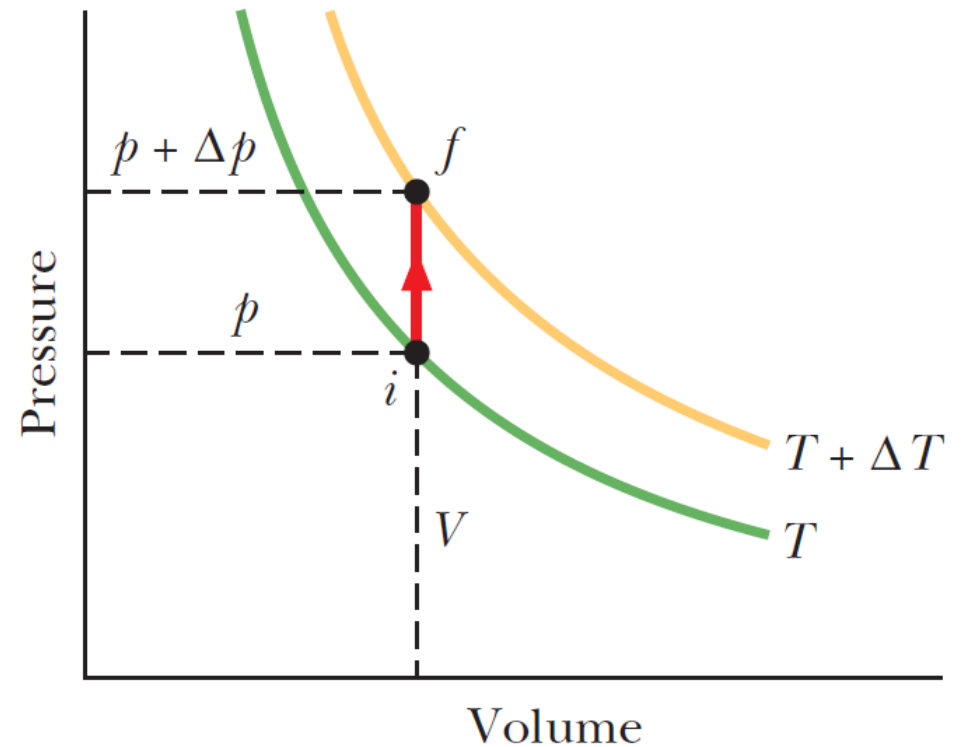
Molar Specific Heat at Constant Volume

Substituting in the first law of thermodynamics yields

$$\Delta E_{\text{int}} = nC_V\Delta T - W,$$

Setting $W = 0$ and solving for C_V we find (for monatomic ideal gas)

$$\begin{aligned} C_V &= \frac{\Delta E_{\text{int}}}{n\Delta T} = \frac{\frac{3}{2}nR\Delta T}{n\Delta T} = \frac{3}{2}R \\ &= 12.5 \text{ J/mol} \cdot \text{K}. \end{aligned}$$



6. The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Volume

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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

6. The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Volume

In **diatomic** and **polyatomic** gases, the molecules can have rotational kinetic energy in addition to the translational kinetic energy.

According to the **equipartition of energy** theorem, the internal energy of a gas is

$$E_{\text{int}} = f \frac{1}{2} nRT,$$

where f is the number of degrees of freedom of a molecule. The corresponding value of C_V is now

$$C_V = \frac{f}{2} R.$$

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

6. The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Volume

A **monatomic** gas molecule has THREE degrees of freedom (3 translational), and thus

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

A **diatomic** gas molecule has FIVE degrees of freedom (3 translational + 2 rotational), and thus

$$C_V = \frac{5}{2}R. \quad (\text{diatomic})$$

A **polyatomic** gas molecule has SIX degrees of freedom (3 translational + 3 rotational), and thus

$$C_V = 3R. \quad (\text{polyatomic})$$

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

6. The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Volume

We can generalize the expression $E_{\text{int}} = 3/2 nRT$ which is for monatomic ideal gases to include di- and poly-atomic ideal gases by replacing $3/2 R$ with C_V . We then get

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

The change of internal energy ΔE_{int} for any ideal gas, due to a temperature change ΔT is given by

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

“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.”

6. The Molar Specific Heats of an Ideal Gas

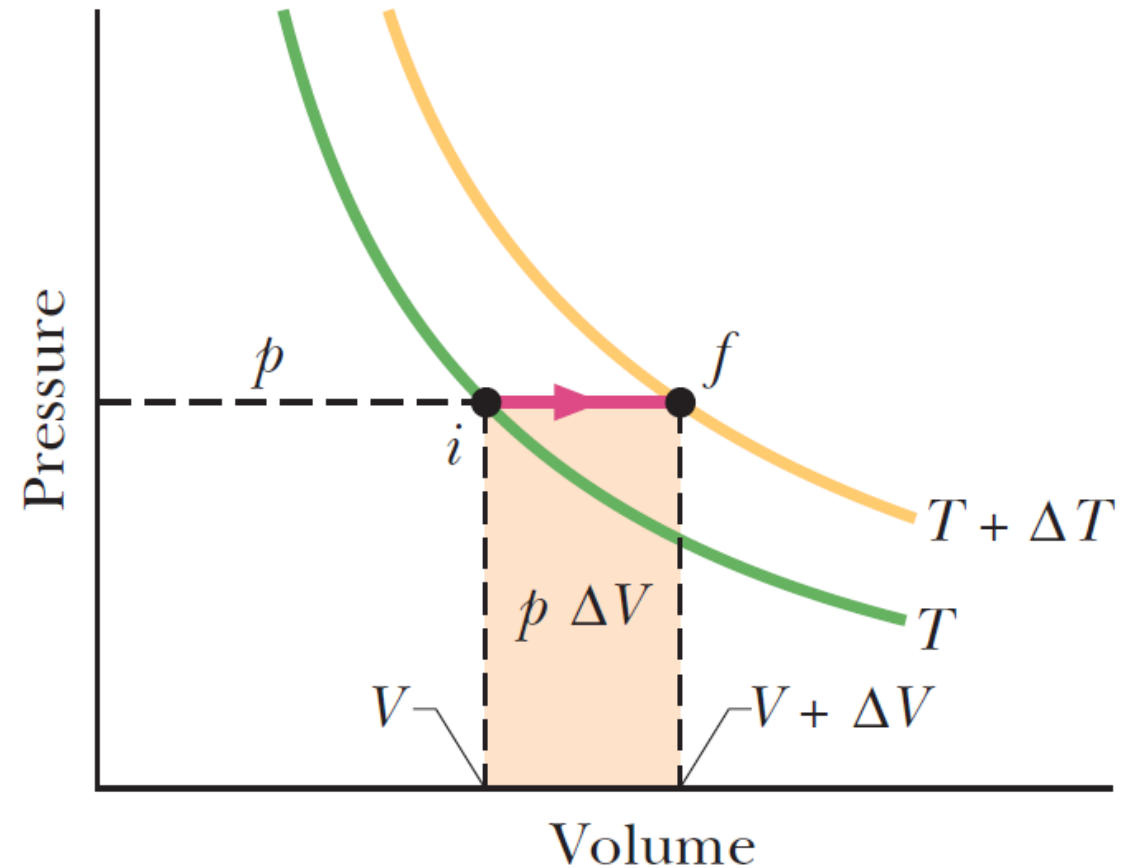
Molar Specific Heat at Constant Pressure

In the process shown in the figure, the temperature of an ideal gas rises to $T + \Delta T$, and the volume rises to $V + \Delta V$ while p is unchanged.

The heat Q added to the gas is related to ΔT by

$$Q = nC_p\Delta T$$

where C_p is the **molar specific heat at constant pressure**.



6. The Molar Specific Heats of an Ideal Gas

Molar Specific Heat at Constant Pressure

C_p is larger than C_V because now the gas does work. Substituting in the first law of thermodynamics gives

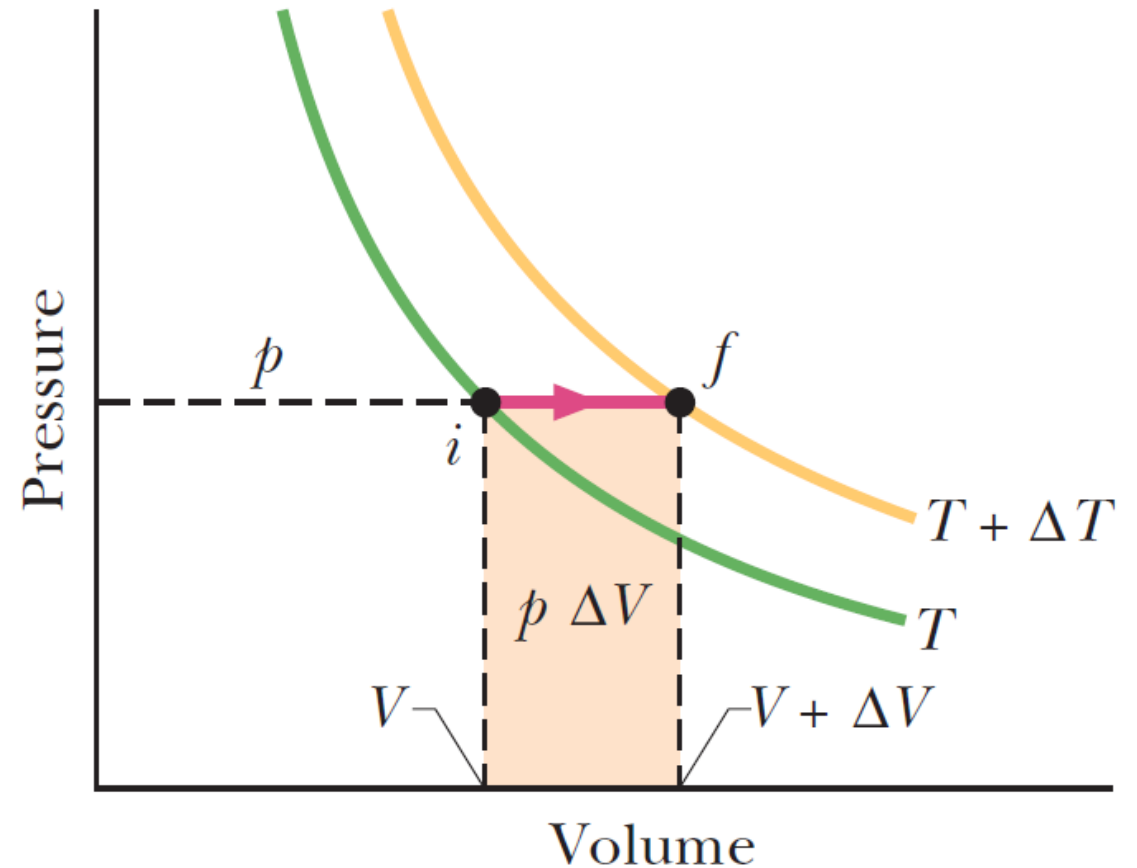
$$\Delta E_{\text{int}} = nC_p\Delta T - W = nC_p\Delta T - p\Delta V.$$

From the ideal gas law ($pV = nRT$), $p\Delta V = nR\Delta T$. We then write

$$\Delta E_{\text{int}} = nC_p\Delta T - nR\Delta T.$$

Solving for C_p gives

$$C_p = \frac{\Delta E_{\text{int}}}{n\Delta T} + R = C_V + R.$$



6. The Molar Specific Heats of an Ideal Gas

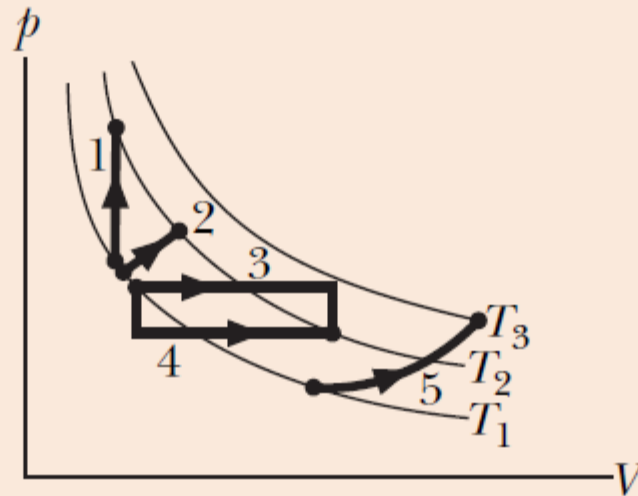
Gas	Degrees of Freedom	E_{int} $(\frac{f}{2}nRT)$	C_V $(\frac{f}{2}R)$	C_p $(C_V + R)$
Monatomic	3	$\frac{3}{2}nRT$	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	5	$\frac{5}{2}nRT$	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	6	$3nRT$	$3R$	$4R$

6. The Molar Specific Heats of an Ideal Gas



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.



5 greatest, then 1, 2, 3 and 4 tie.

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

6. The Molar Specific Heats of an Ideal Gas

Example 4: A bubble of 5.00 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 20.0 C° at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

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

$$Q = nC_p\Delta T = n\left(\frac{5}{2}R\right)\Delta T = (5.00 \text{ mol})\left(\frac{5}{2}8.31\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(20.0\text{C}^\circ) = 2.08 \text{ kJ.}$$

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

$$\Delta E_{\text{int}} = nC_v\Delta T = \frac{3}{2}nR\Delta T = (5.00 \text{ mol})\left(\frac{3}{2}8.31\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(20.0\text{C}^\circ) = 1.25 \text{ kJ.}$$

6. The Molar Specific Heats of an Ideal Gas

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

$$W = p\Delta V = nR\Delta T = (5.00 \text{ mol}) \left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (20.0\text{C}^\circ) = 831 \text{ J}.$$

Another way:

$$W = Q - \Delta E_{\text{int}} = 2.0775 \text{ kJ} - 1.2465 \text{ kJ} = 831 \text{ J}.$$

7. The adiabatic Expansion of an Ideal Gas

In adiabatic processes $Q = 0$. We can make $Q = 0$ by carrying out the process very quickly or in a well insulated container.

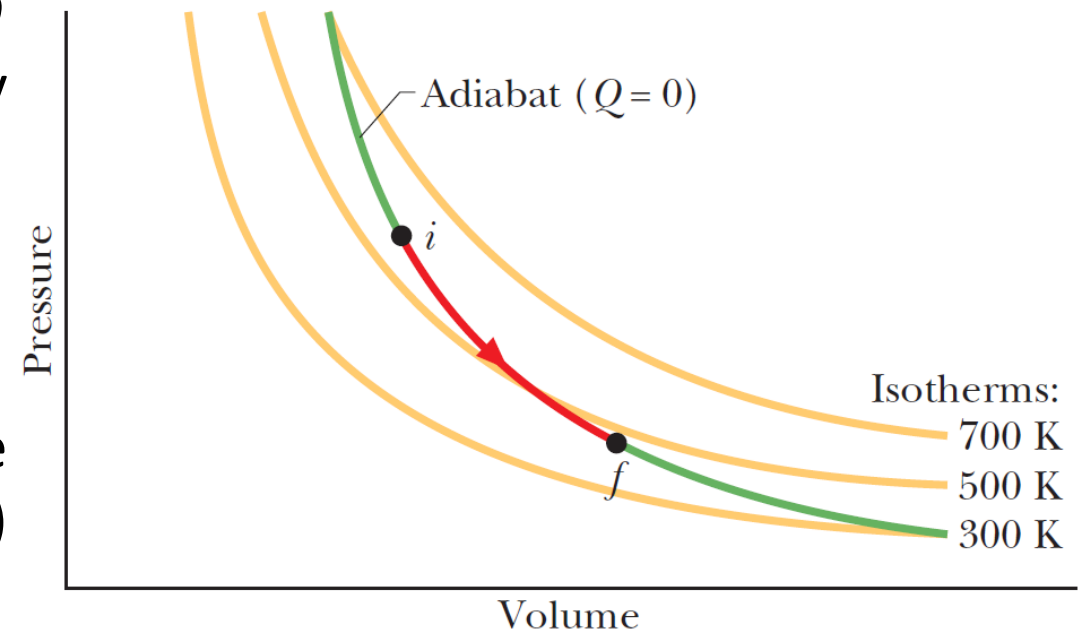
During an adiabatic process

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

where $\gamma = C_p/C_V$. On the p - V diagram, the process occurs along a line (called an **adiabat**) that has the equation $p = \text{a constant}/V^\gamma$.

When the gas goes from state i to state f

$$p_i V_i^\gamma = p_f V_f^\gamma.$$



7. The adiabatic Expansion of an Ideal Gas

Using the ideal gas law, we can write

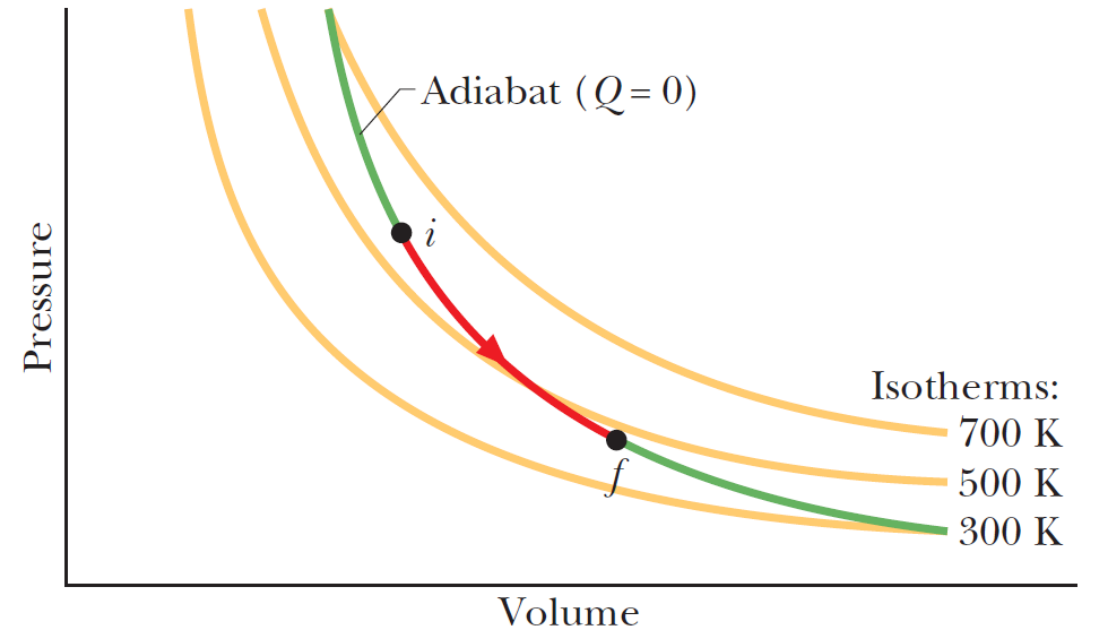
$$\left(\frac{nRT}{V}\right)V^\gamma = \text{a constant},$$

or

$$TV^{\gamma-1} = \text{a constant. (new constant)}$$

When the gas goes from state i to state f ,

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}.$$



7. The adiabatic Expansion of an Ideal Gas

Free Expansions

A free expansion is an adiabatic process with no work or change in internal energy.

In free expansions the system is in equilibrium only at the initial and final states.

We do not know the state of the gas in between.

Because $\Delta E_{\text{int}} = 0$, $\Delta T = 0$ or

$$T_i = T_f.$$

Using $pV = nRT$ yields

$$p_i V_i = p_f V_f.$$

7. The adiabatic Expansion of an Ideal Gas

Example 5: Initially, 1 mol of neon (assumed to be an ideal gas) has temperature $T_i = 310$ K and volume $V_i = 12.0$ L. We will allow it to expand to volume $V_f = 19.0$ L.

(a) What would be the final temperature if the gas expands adiabatically?

The initial and final temperatures and volumes of the gas are related by

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}.$$

with

$$\gamma = \frac{C_p}{C_V} = \frac{5/2 R}{3/2 R} = 1.60.$$

Solving for T_f and substituting gives

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1} = (310 \text{ K}) \left(\frac{12.0 \text{ L}}{19.0 \text{ L}} \right)^{1.60-1} = 235 \text{ K}.$$

7. The adiabatic Expansion of an Ideal Gas

(b) What would be the final temperature and pressure if, instead, the gas expands freely to the new volume, from an initial pressure of 2.00 Pa?

The temperature does not change in free expansions. We also know that, for a free expansion

$$p_i V_i = p_f V_f.$$

The final pressure is therefore

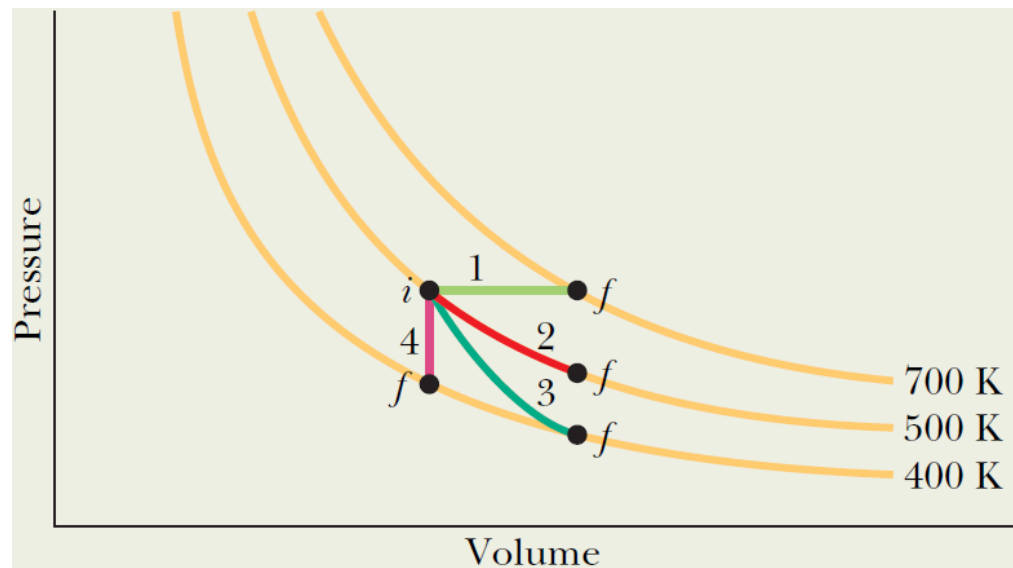
$$p_f = \frac{p_i V_i}{V_f} = \frac{(2.00 \text{ Pa})(12.0 \text{ L})}{(19.0 \text{ L})} = 1.26 \text{ Pa}.$$

7. The adiabatic Expansion of an Ideal Gas



CHECKPOINT 5

Rank paths 1, 2, and 3 in Fig. 19-16 according to the energy transfer to the gas as heat, greatest first.



1, 2, then 3.

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

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

Four Special Processes

			Some Special Results
Path in Fig. 19-16	Constant Quantity	Process Type	($\Delta E_{\text{int}} = Q - W$ 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	$pV^\gamma, TV^{\gamma-1}$	Adiabatic	$Q = 0; W = -\Delta E_{\text{int}}$
4	V	Isochoric	$Q = \Delta E_{\text{int}} = nC_V\Delta T; W = 0$

