



Thermodynamics Molecular Model of a Gas Molar Heat Capacities (Monatomic Gases)

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Last time

- heat transfer mechanisms: radiation
- modeling an ideal gas at the microscopic level
- pressure, temperature, and internal energy from microscopic model

Overview

- modeling an ideal gas at the microscopic level
- rms speed of molecules
- equipartition of energy
- heat capacities for ideal gases

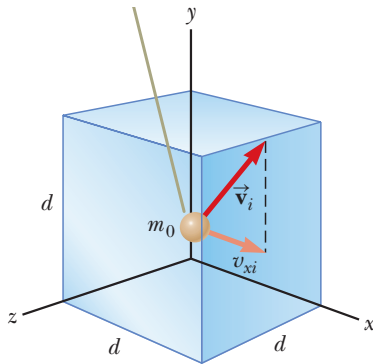
Kinetic Theory of Gases

Previously, we studied what happens in thermodynamic systems to bulk properties in various transformations.

Now we want to understand how these macroscopic quantities arise from the microscopic behavior of particles, *on average*.

We cannot model every the motion of every single particle in a substance, but we can say a lot about the **ensemble** of particles statistically.

Molecular Model of an Ideal Gas



We modeled the particles of gas as small, identical, and obeying Newton's laws, with no long range interactions.

We assumed all collisions are elastic.

¹Figure from Serway & Jewett.

Pressure from the Molecular Model

Pressure, P , can be related to the average translational kinetic energy, \bar{K}_{trans} , of the molecules of a gas.

$$P = \frac{2}{3} \frac{N}{V} \bar{K}_{\text{trans}}$$

More K.E., or more molecules in less volume \Rightarrow higher pressure.

Relation to Macroscopic view of an Ideal Gas

Ideal gas equation:

$$PV = nRT$$

or equivalently:

$$PV = Nk_B T$$

If we put our new expression for pressure into this equation:

$$\frac{2}{3} N \bar{K}_{\text{trans}} = Nk_B T$$

We can cancel N from both sides and re-arrange:

$$\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

Temperature from the Molecular Model

We can also relate temperature to molecular motion!

$$T = \frac{2}{3k_b} \bar{K}_{\text{trans}}$$

Temperature is directly proportional to the translational kinetic energy of the particles.

RMS Speed and Temperature

$$\bar{K} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

It would also be useful to express the average molecular speed in terms of the temperature.

Since the motion of the gas molecules are isotropic, the average velocity is zero.

However, we can instead consider the **root-mean-square (rms) speed**.

That is convenient here because we have the average of the squares of the speed, not the average speed itself.

RMS Speed and Temperature

root-mean-square (rms) speed:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}}$$

Alternatively, it can be expressed

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

where M is the molar mass.

rms speed is higher for less massive molecules for a given temperature.

RMS Speed Question

An ideal gas is maintained at constant pressure. If the temperature of the gas is increased from 200 K to 600 K, what happens to the rms speed of the molecules?

- (A) It increases by a factor of 3.
- (B) It remains the same.
- (C) It is one-third the original speed.
- (D) It is $\sqrt{3}$ times the original speed.

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Equipartition of Energy

In physics, the number of **degrees of freedom** a system has is the number of real number variables we need to specify to describe a system.

For our purposes here, we can say that each degree of freedom counts another way that a particle can possess energy.

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For our purposes here, we can say that each degree of freedom counts another way that a particle can possess energy.

It can move in the x-direction, having kinetic energy, but also in the y and z directions. That's 3 ways. 3 degrees of freedom.

Degrees of freedom count rotational and vibrational motion as well as translational K.E.

Equipartition of energy theorem

Each degree of freedom for a molecule contributes an additional $\frac{1}{2}k_B T$ of energy to the system.

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It can be proven starting from the Boltzmann distribution of energies (to come).

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This assumes a continuum of possible energies, so we expect problems when we are in settings where the thermal energy $k_B T$ is much less than the energy spacing between energy levels predicted by quantum mechanics.

Kinetic Energy and Internal Energy

The total kinetic energy of an ideal **monatomic** gas of N particles is the total translational K.E.

$$K_{\text{tot,trans}} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

In a **monatomic** gas these are the three translational motions are the only degrees of freedom. We can choose

$$E_{\text{int}} = K_{\text{tot,trans}} = N \left(\frac{3}{2} k_B T \right) = \frac{3}{2} n R T$$

(This is the thermal energy, so the bond energy is zero – if we liquify the gas the bond energy becomes negative.)

Question

Quick Quiz 21.1¹ Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.

(i) What is the average translational kinetic energy per molecule in container B?

- (A) twice that of container A
- (B) the same as that of container A
- (C) half that of container A
- (D) impossible to determine

¹Serway & Jewett, page 631.

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(ii) From the same choices, describe the internal energy of the gas in container B.

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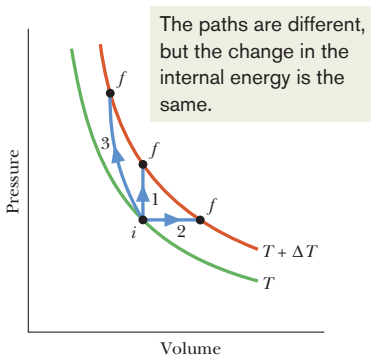
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Another Look at Heat Capacity

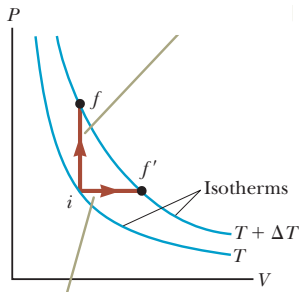
We already studied specific heat, $c = \frac{Q}{m\Delta T}$, particularly for solids and liquids.

Now we must revisit this concept, because for gases there are many ways to change the temperature of a gas by ΔT , with different ways requiring different amounts of heat, Q .



¹Diagram from Halliday, Resnick, Walker, 9th ed, page 520.

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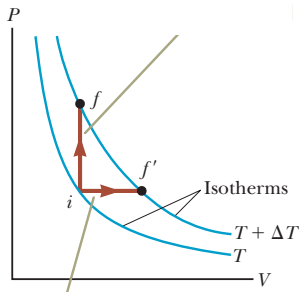


Quick Quiz 21.2² (i) How does the internal energy of an ideal gas change as it follows path $i \rightarrow f$?

- (A) E_{int} increases.
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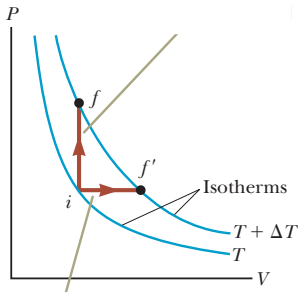


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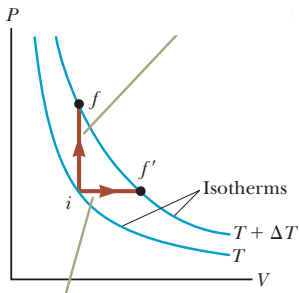


Quick Quiz 21.2² (ii) From the same choices, how does the internal energy of an ideal gas change as it follows path $f \rightarrow f'$ along the isotherm labeled $T + \Delta T$?

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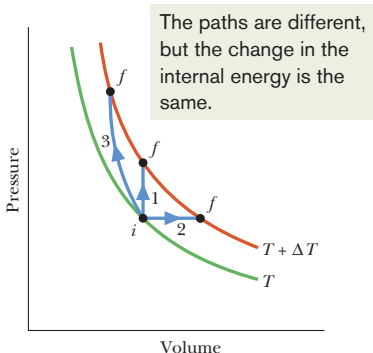
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Another Look at Heat Capacity

Paths with the same ΔT ,
 ΔE_{int} :



We have related internal energy to temperature through KE (monatomic gas):

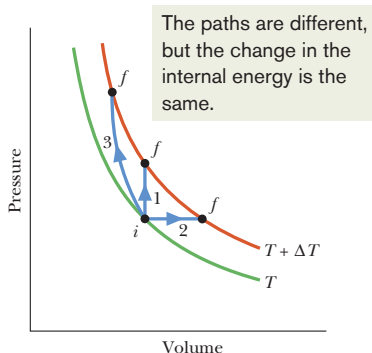
$$E_{\text{int}} = K_{\text{tot,trans}} = \frac{3}{2}nRT$$

and from the first law of thermodynamics:

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

Since W is different for the different processes shown, so is Q .

Another Look at Heat Capacity



For processes 1, 2, and 3:

$$Q_1 = c_1 m \Delta T$$

$$Q_2 = c_2 m \Delta T$$

$$Q_3 = c_3 m \Delta T$$

Each process has a different value of c !

Molar Specific Heat of an Ideal Gas

For solids and liquids, heat capacity, C , and specific heat capacity, c , are defined to be for **constant pressure** processes.

This is purely because it is very difficult to stop a solid or liquid from expanding and maintain it at a constant volume!

$$(\Delta V = \beta V_i \Delta T)$$

However, it is possible to measure the heat capacities of solids and liquids at constant volume instead of constant pressure.

When that is done, small differences in the values of the heat capacity are obtained.

Molar Specific Heat of an Ideal Gas

In gases, the variation of the heat capacity obtained for different paths is quite big.

Define:

Molar heat capacity at constant volume, C_V

Along an isovolumetric process (constant volume):

$$Q = nC_V \Delta T$$

Molar heat capacity at constant pressure, C_P

Along an isobaric process (constant pressure):

$$Q = nC_P \Delta T$$

(These are both *intensive* quantities, like specific heat.)

Molar Specific Heat of an Ideal Gas

We have defined **molar** heat capacities (cap. per mole) here and not specific heat capacities (cap. per mass).

Why?

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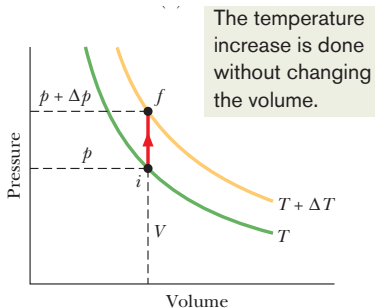
Why?

Using “per mole” as the reference for heat capacity allows us to talk about many different gases with the same relationships, since we will always be talking about the same number of molecules.

It is just more convenient.

Heat Capacity for Constant Volume Processes

In a constant volume process, no work is done: $\Delta E_{\text{int}} = Q$



Therefore,

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

and

$$C_V = \frac{1}{n} \left(\frac{\partial E_{\text{int}}}{\partial T} \right)_V \quad (\text{the subscript } V \text{ means const volume})$$

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Putting in our value for internal energy:

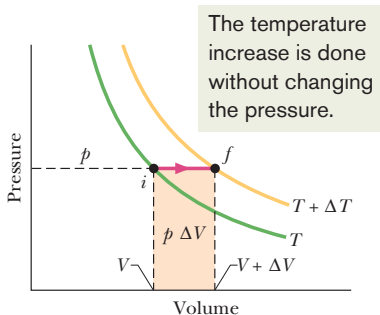
$$\begin{aligned} C_V &= \frac{1}{n} \left(\frac{\partial}{\partial T} \left(\frac{3}{2} nRT \right) \right)_V \\ C_V &= \frac{3}{2} R \end{aligned}$$

This is the value for C_V for *all monatomic gases*.

Heat Capacity for Constant Pressure Processes

In a constant pressure process, the work done on the gas is:

$$W = -P \Delta V$$



From the ideal gas equation:

$$P \Delta V = nR \Delta T$$

So,

$$W = -nR \Delta T$$

Heat Capacity for Constant Pressure Processes

First law:

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

rearranging:

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

$$nC_V \Delta T - nC_P \Delta T = -nR \Delta T$$

Heat Capacity for Constant Pressure Processes

First law:

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

rearranging:

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

$$nC_V \Delta T - nC_P \Delta T = -nR \Delta T$$

because $Q = nC_P \Delta T$. Dividing by $-n\Delta T$:

$$C_P - C_V = R$$

For a **monatomic** gas:

$$C_P = \frac{5}{2}R$$

Summary

- molecular models
- rms speed of molecules
- equipartition of energy
- molar heat capacities

Quiz in class, Friday.

Collected Homework due Monday, May 7.

Test on Thermodynamics, discuss date! - Monday, May 14.

Homework Serway & Jewett:

- new: Ch 21, CQs: 7; Probs: 15, 17, 21, 23, 25, 29, 31, 47, 59, 65