Thermodynamics
Molecular Model of a Gas
Molar Heat Capacities

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Last time

- heat capacities for monatomic ideal gases

Overview

- heat capacities for diatomic ideal gases
- adiabatic processes

Quick Recap

For all ideal gases:

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

and

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

For monatomic gases:

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

and so,

$$C_V = \frac{3}{2}R$$

and

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

Reminder: Kinetic Energy and Internal Energy

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

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

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

Equipartition Consequences in Diatomic Gases

Reminder:

Equipartition of energy theorem

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

A monatomic gas has 3 degrees of freedom: it can have translational KE due to motion in 3 independent directions.

A diatomic gas has more ways to move and store energy.

It can:

- translate
- rotate
- vibrate

Equipartition Consequences in Diatomic Gases

Contribution to internal energy:

$$3\left(\frac{1}{2}k_B T\right) \longrightarrow$$

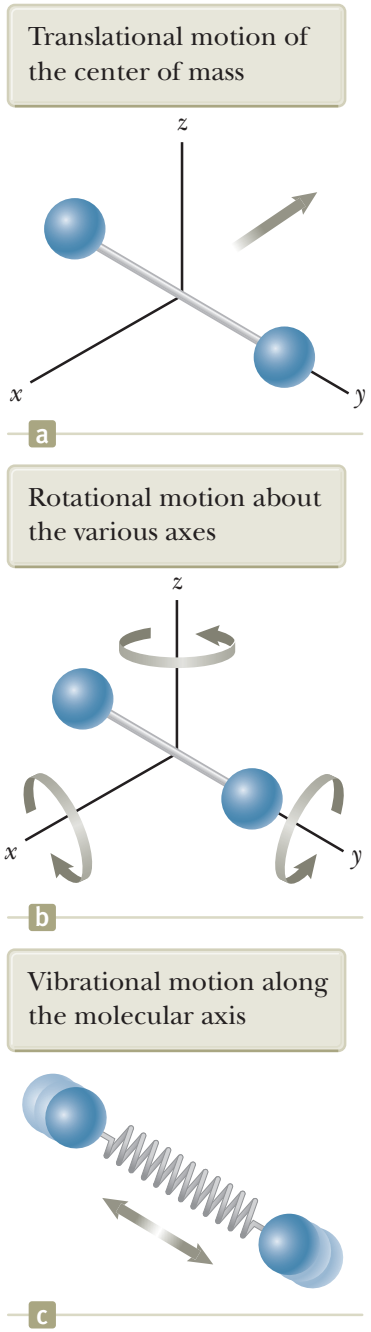
(3 directions of motion)

$$2\left(\frac{1}{2}k_B T\right) \longrightarrow$$

(rotations about x and z axes)

$$2\left(\frac{1}{2}k_B T\right) \longrightarrow$$

(KE and PE of harmonic oscillator)



(Classical) Equipartition Prediction for Diatomic Gases

In total:

$$E_{\text{int}} = N\left(\frac{7}{2}k_B T\right)$$

We can also write the internal energy:

$$E_{\text{int}} = \frac{7}{2}nRT$$

And so,

$$C_V = \frac{7}{2}R$$

This is what we would expect for a diatomic gas based on the equipartition theorem.

It is not quite what is observed, however.

What Actually Happens in Diatomic Gases

Prediction:

$$C_V = \frac{7}{2}R$$

For most diatomic gases, such as H_2 and N_2,

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

at moderate temperatures (around room temperature).

And at low temperatures for these gases $C_V = \frac{3}{2}R$.

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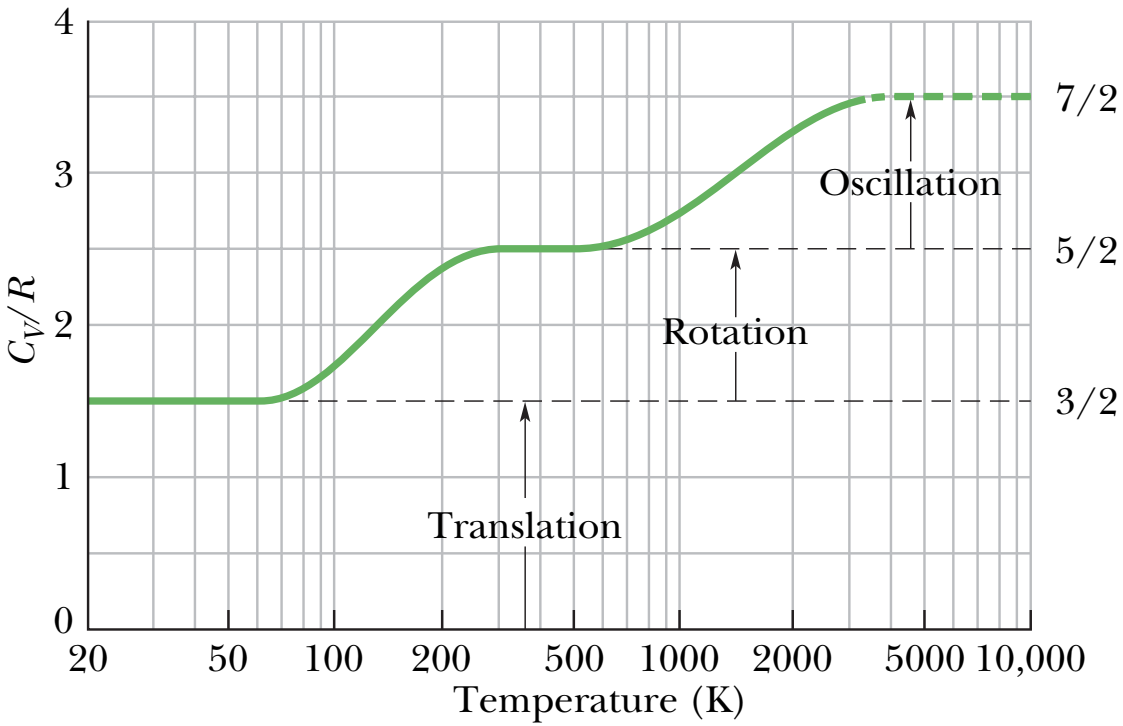
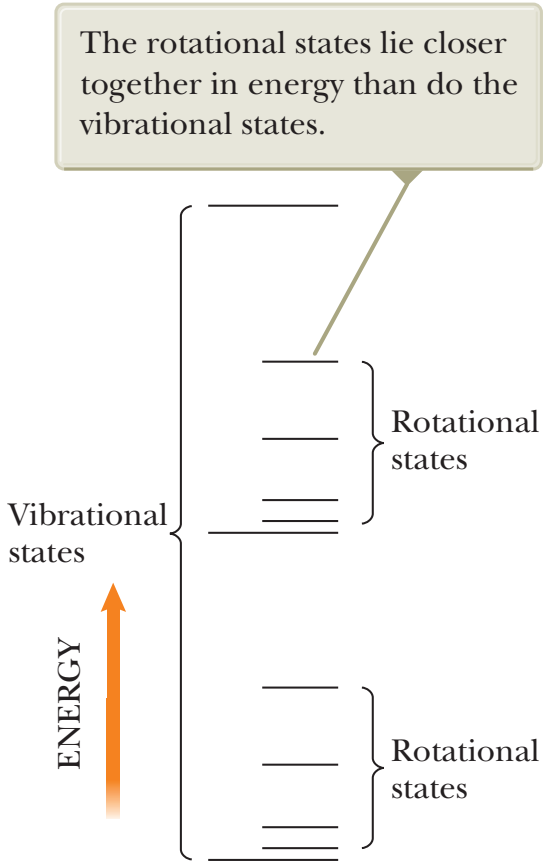
It is almost as if degrees of freedom become "activated" once there is enough energy...

What Actually Happens in Diatomic Gases

Hydrogen gas:





At 3200K the molecules begin to dissociate.

[1]Left diagram, Halliday, Resnick, Walker; right diagram Serway & Jewett

Question

Quick Quiz 21.4[1] The molar specific heat of a gas is measured at constant volume and found to be $11R/2$. Is the gas most likely to be

(A) monatomic,

(B) diatomic, or

(C) polyatomic?

[1] Serway & Jewett, page 637.

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A Useful Ratio

The quantity γ is defined as:

$$\gamma = \frac{C_P}{C_V}$$

For a monatomic gas:

$$\gamma = \frac{5}{3}$$

What is γ for a diatomic gas near room temperature?

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Summary of Results

For ideal gases at moderate temperatures (around room temperature):

	monatomic gas	diatomic gas
C_V	$\frac{3}{2}R$	$\frac{5}{2}R$
C_P	$\frac{5}{2}R$	$\frac{7}{2}R$
$\gamma = \frac{C_P}{C_V}$	$\frac{5}{3}$	$\frac{7}{5}$

Adiabatic Process in Ideal Gases

For an adiabatic process ($Q = 0$):

$$PV^{\gamma} = \text{const.}$$

and:

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

Adiabatic Process in Ideal Gases

For an adiabatic process ($Q = 0$):

$$PV^{\gamma} = \text{const.}$$

and:

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

(Given the first one is true, the second follows immediately from the ideal gas equation, $P = \frac{nRT}{V}$.)

Adiabatic Process in Ideal Gases

Where this relation comes from:

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

Considering a small volume change in time that produces a small change in temperature:

$$\begin{aligned} \frac{\mathrm{dE_{int}}}{\mathrm{dt}} &= \frac{\mathrm{dW}}{\mathrm{dt}} \\ nC_V \frac{\mathrm{dT}}{\mathrm{dt}} &= -P \frac{\mathrm{dV}}{\mathrm{dt}} \end{aligned} \tag{1}$$

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The ideal gas law ($PV = nRT$) derivative:

$$\begin{aligned} P \frac{\mathrm{dV}}{\mathrm{dt}} + V \frac{\mathrm{dP}}{\mathrm{dt}} &= nR \frac{\mathrm{dT}}{\mathrm{dt}} \\ n \frac{\mathrm{dT}}{\mathrm{dt}} &= \frac{1}{R} \left(P \frac{\mathrm{dV}}{\mathrm{dt}} + V \frac{\mathrm{dP}}{\mathrm{dt}} \right) \end{aligned}$$

Substitute $n \frac{\mathrm{dT}}{\mathrm{dt}}$ into our energy equation (1).

Adiabatic Process in Ideal Gases

$$
\begin{aligned}
C_V \left(n \frac{\mathrm{dT}}{\mathrm{dt}} \right) &= -P \frac{\mathrm{dV}}{\mathrm{dt}} \\
\frac{C_V}{R} \left(P \frac{\mathrm{dV}}{\mathrm{dt}} + V \frac{\mathrm{dP}}{\mathrm{dt}} \right) &= -P \frac{\mathrm{dV}}{\mathrm{dt}} \\
V \frac{\mathrm{dP}}{\mathrm{dt}} &= -\left(1 + \frac{R}{C_V} \right) P \frac{\mathrm{dV}}{\mathrm{dt}}
\end{aligned}
$$

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Notice: $\gamma = 1 + \dfrac{R}{C_V}$

then, dividing by PV:

$$\frac{1}{P}\,\frac{\mathrm{dP}}{\mathrm{dt}} = -\frac{\gamma}{V}\,\frac{\mathrm{dV}}{\mathrm{dt}}$$

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Integrating both sides:

$$\ln P = -\gamma \ln V + c$$

Adiabatic Process in Ideal Gases

$$\ln P = -\gamma \ln V + c$$

Implies:

$$PV^{\gamma} = \text{const.}$$

This equation characterizes an adiabatic process in an ideal gas, along with this one, which follows from $PV = nRT$:

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

Example

Based on problem 28, Chapter 21.

How much work is required to compress 5.00 mol of air at 20.0°C and 1.00 atm to one-tenth of the original volume in an adiabatic process? Assume air behaves as an ideal diatomic-type gas.

[1] Serway & Jewett, page 647.

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One way:

$$PV^{\gamma} = P_i V_i^{\gamma}$$

and

$$W = -\int P \, \mathrm{dV}$$

Another way:

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

and

$$W = \Delta E_{\text{int}} - \cancelto{0}{Q} = nC_V \Delta T$$

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$$W = \Delta E_{\text{int}} - \cancelto{0}{Q} = nC_V \Delta T$$

$$W = 46.0 \text{ kJ}$$

[1] Serway & Jewett, page 647.

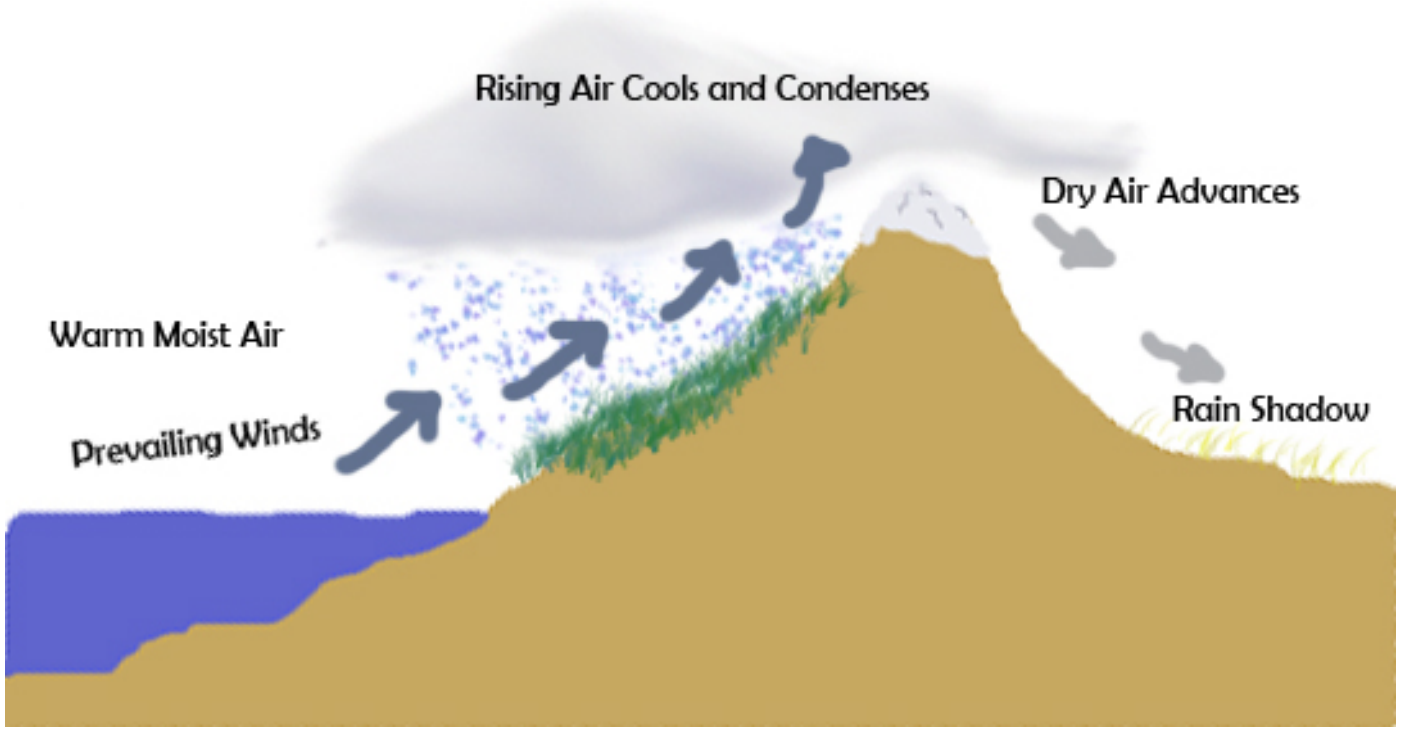
Weather and Adiabatic Process in a Gas

On the eastern side of the Rocky Mountains there is a phenomenon called chinooks.

These eastward moving wind patterns cause distinctive cloud patterns (chinook arches) and sudden increases in temperature.

Weather and Adiabatic Process in a Gas

As the air rises from the ocean it expands in the lower pressure at altitude and cools. The water vapor condenses out of the air and falls as precipitation.



As the air passes over the mountain it absorbs the latent heat from the water condensation, then it stops cooling. As it descends, it is compressed (nearly) adiabatically as the ambient pressure increases. The air temperature rises!

Summary

- more equipartition of energy
- molar heat capacities
- adiabatic processes

Homework

- Full-solution HW2, due tomorrow
- WebAssign, due tomorrow

Serway & Jewett (additional problems you might like to look at):

- Ch 21, Probs: 52, 58, 65