



Thermodynamics

Molecular Model of a Gas

Molar Heat Capacities

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Last time

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

Overview

- constant-pressure heat capacity for monatomic gases
- 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:

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

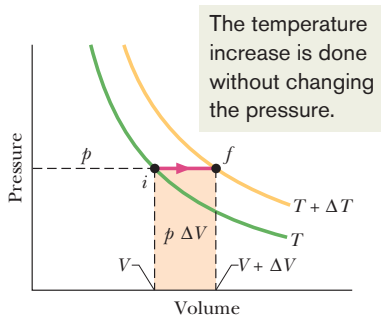
and so,

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

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:

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

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.)

Equipartition Consequences in Diatomic Gases

Reminder:

Equipartition of energy theorem

Each degree of freedom for each molecule contributes an 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:

$$\frac{3}{2}k_B T \rightarrow$$

(3 directions of motion)

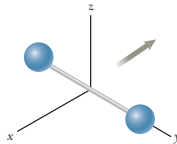
$$\frac{2}{2}k_B T \rightarrow$$

(rotations about x and z axes)

$$\frac{2}{2}k_B T \rightarrow$$

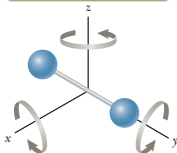
(KE and PE of harmonic oscillator)

Translational motion of the center of mass



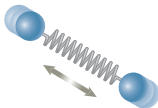
a

Rotational motion about the various axes



b

Vibrational motion along the molecular axis



c

(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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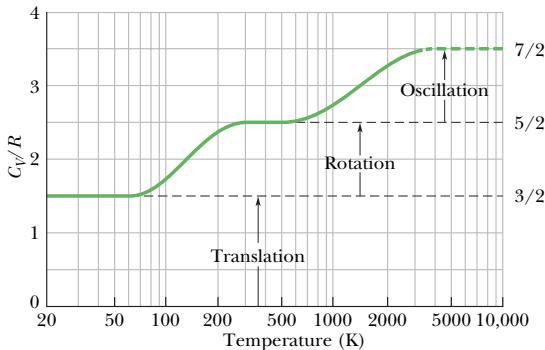
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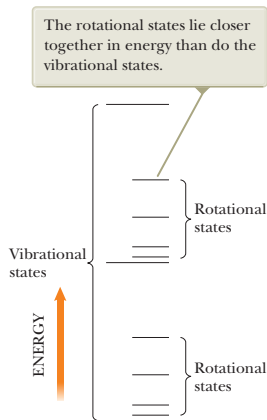
It is almost as if degrees of freedom become “activated” once there is enough energy...

What Actually Happens in Diatomic Gases

Hydrogen gas:



At 3200K the molecules begin to dissociate.



Question

Quick Quiz 21.4¹ 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?

¹Serway & 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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$$\gamma = \frac{7}{5}$$

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:

$$nC_V \frac{dT}{dt} = -P \frac{dV}{dt} = \frac{dE_{\text{int}}}{dt} = \frac{dW}{dt} \quad (1)$$

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:

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

The ideal gas law derivative:

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

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

Adiabatic Process in Ideal Gases

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

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

then, dividing by PV :

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

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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 $PV = nRT$:

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

Summary

- equipartition of energy
- molar heat capacities
- adiabatic processes

Quiz in class, Friday.

Collected Homework due Monday, May 7.

Test on Thermodynamics, Monday, May 14.

Homework Serway & Jewett:

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