Specific Heat of Diatomic Gases and Solids

The Adiabatic Process

Ron Reifenberger
Birck Nanotechnology Center
Purdue University
February 22, 2012
Specific Heat for Solids and Diatomic Gasses

In this lecture, you will learn what determines the specific heat of diatomic gasses and elemental solids.

The physics behind an adiabatic gas process will also be analyzed.
From last lecture, you learned how to evaluate the heat capacity for an ideal monatomic gas

$$ KE_{av} = K_{av} = \frac{1}{2} m \left( v_{av}^2 \right) = 3 \left( \frac{1}{2} kT \right) \quad \text{(for one molecule)} $$

The internal energy of N atoms in an ideal monatomic gas is an intrinsic, distributed property of the system.

For ideal gas of N atoms:

$$ E_{int} \rightarrow KE = 3 \left( \frac{1}{2} NkT \right) = 3 \left( \frac{1}{2} nRT \right) $$

$$ C_V \equiv \frac{dE_{int}}{dT} = \frac{3}{2} nR $$

$$ C_p = C_V + nR = \frac{5}{2} nR $$

What makes diatomic molecules different?
Rotational motion - another way to distribute energy?

\[ KE = \frac{1}{2} \, m v^2 \]
\[ \omega = 2\pi f \]
\[ v = r\omega \]

\[ KE = \frac{1}{2} \, m r^2 \, \omega^2 = \frac{1}{2} \, I \, \omega^2 \]

Typical value: CO, \( I \approx 1.45 \times 10^{-46} \) kg\( \cdot \)m\(^2\)
By way of review, . . .

<table>
<thead>
<tr>
<th></th>
<th>Linear Motion</th>
<th>Rotational Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Displacement</strong></td>
<td>( d = v_0 t + \frac{1}{2} at^2 )</td>
<td>( \theta = \omega_0 t + \frac{1}{2} \alpha t^2 )</td>
</tr>
<tr>
<td><strong>Velocity</strong></td>
<td>( v = v_0 + at )</td>
<td>( \omega = \omega_0 + \alpha t )</td>
</tr>
<tr>
<td><strong>Inertia</strong></td>
<td>( m )</td>
<td>( I )</td>
</tr>
<tr>
<td><strong>Newton's 2\textsuperscript{nd} Law</strong></td>
<td>( \vec{F} = m \vec{a} )</td>
<td>( \vec{\tau} = I \vec{\alpha} )</td>
</tr>
<tr>
<td><strong>Momentum</strong></td>
<td>( \vec{p} = mv )</td>
<td>( \vec{L} = I \vec{\omega} )</td>
</tr>
<tr>
<td><strong>Conservation of momentum</strong></td>
<td>If ( F=0 ), then ( p = \text{constant} )</td>
<td>If ( \tau=0 ), then ( L = \text{constant} )</td>
</tr>
<tr>
<td><strong>Kinetic Energy</strong></td>
<td>( \frac{1}{2} mv^2 )</td>
<td>( \frac{1}{2} I\omega^2 )</td>
</tr>
</tbody>
</table>
For diatomic molecules, additional energy can be disbursed in rotational motion.

\[
\begin{align*}
\text{KE} &= \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 \\
E_{\text{int}} &= 5 \left( \frac{1}{2} nRT \right) \rightarrow C_v = \frac{5}{2} nR \rightarrow C_p = \frac{7}{2} nR
\end{align*}
\]
### TABLE 18-3

Molar Heat Capacities in J/mol-K of Various Gases at 25°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>$c'_p$</th>
<th>$c'_v$</th>
<th>$c'_v/R$</th>
<th>$c'_p - c'_v$</th>
<th>$(c'_p - c'_v)/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monatomic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>20.79</td>
<td>12.52</td>
<td>1.51</td>
<td>8.27</td>
<td>0.99</td>
</tr>
<tr>
<td>Ne</td>
<td>20.79</td>
<td>12.68</td>
<td>1.52</td>
<td>8.11</td>
<td>0.98</td>
</tr>
<tr>
<td>Ar</td>
<td>20.79</td>
<td>12.45</td>
<td>1.50</td>
<td>8.34</td>
<td>1.00</td>
</tr>
<tr>
<td>Kr</td>
<td>20.79</td>
<td>12.45</td>
<td>1.50</td>
<td>8.34</td>
<td>1.00</td>
</tr>
<tr>
<td>Xe</td>
<td>20.79</td>
<td>12.52</td>
<td>1.51</td>
<td>8.27</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Diatominc</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>29.12</td>
<td>20.80</td>
<td>2.50</td>
<td>8.32</td>
<td>1.00</td>
</tr>
<tr>
<td>H₂</td>
<td>28.82</td>
<td>20.44</td>
<td>2.46</td>
<td>8.38</td>
<td>1.01</td>
</tr>
<tr>
<td>O₂</td>
<td>29.37</td>
<td>20.98</td>
<td>2.52</td>
<td>8.39</td>
<td>1.01</td>
</tr>
<tr>
<td>CO</td>
<td>29.04</td>
<td>20.74</td>
<td>2.49</td>
<td>8.30</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Polyatomic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>36.62</td>
<td>28.17</td>
<td>3.39</td>
<td>8.45</td>
<td>1.02</td>
</tr>
<tr>
<td>N₂O</td>
<td>36.90</td>
<td>28.39</td>
<td>3.41</td>
<td>8.51</td>
<td>1.02</td>
</tr>
<tr>
<td>H₂S</td>
<td>36.12</td>
<td>27.36</td>
<td>3.29</td>
<td>8.76</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Any other way to distribute energy?

vibrational motion

Work Done = Change in Elastic Energy

\[ W = F \cdot d \]

\[ = \frac{1}{2} \cdot kx \cdot x \]

Work done is equal to the area
It is possible that diatomic molecules may vibrate! Usually, this occurs at temperatures much higher than room temperature. If vibration becomes important, then additional energies must be added to heat capacity to include this possibility.

1 mole of $\text{H}_2$ gas

\[
\begin{align*}
    \text{C}_p &= \frac{7}{2}nRT \\
    &= \frac{5}{2}nRT \\
    &= \frac{3}{2}nRT
\end{align*}
\]
To calculate the specific heat for ELEMENTAL solids, we need a model that describes how atoms interact with each other.

\[ KE = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}kx^2 + \frac{1}{2}ky^2 + \frac{1}{2}kz^2 \]

6 degrees of freedom

\[ E_{\text{int}} = 6 \left( \frac{1}{2} \, nRT \right) \]

for one mole, \( n=1 \)

\[ c \, (\text{molar specific heat}) = 3R \]

\[ c \approx 24.9 \, \text{J/mole K} \]

Law of Dulong-Petit
<table>
<thead>
<tr>
<th>Elemental Solid</th>
<th>$C_V$ (J/mole K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>23.4</td>
</tr>
<tr>
<td>Bismuth</td>
<td>25.3</td>
</tr>
<tr>
<td>Copper</td>
<td>23.8</td>
</tr>
<tr>
<td>Gold</td>
<td>24.5</td>
</tr>
<tr>
<td>Platinum</td>
<td>25.4</td>
</tr>
<tr>
<td>Silver</td>
<td>24.4</td>
</tr>
<tr>
<td>Tungsten</td>
<td>24.4</td>
</tr>
</tbody>
</table>

Dulong-Petit value

$c \approx 24.9$ J/mole K
A Thermodynamic Process: How you go from initial to final state

There are many ways to go from \((P_1, V_1, T_1)\) to \((P_2, V_2, T_2)\)
How to measure P-V for a gas?
The Adiabatic Process for an Ideal Gas

“αδιαβατος” is the Greek word for impassable

Adiabatic Thermodynamic Process
- fast!
- no time for heat to flow in or out

Quasi-static Adiabatic Process
- slow!
- insulation
- no heat flows in or out

\[ \Delta E_{\text{int}} = Q_{\text{in}} + W_{\text{on}} \]
Using the 1st Law for Ideal Monatomic Gas

<table>
<thead>
<tr>
<th>Process</th>
<th>$\Delta E_{int}$</th>
<th>$Q_{in}$</th>
<th>$W_{on}$ =</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobaric</td>
<td>$nc'_v\Delta T$</td>
<td>$nC_p\Delta T$</td>
<td>$-P\Delta V$</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>$nc'_v\Delta T$</td>
<td>0</td>
<td>$\Delta E_{int}$</td>
</tr>
<tr>
<td>Isochoric</td>
<td>$nc'_v\Delta T$</td>
<td>$\Delta E_{int}$</td>
<td>0</td>
</tr>
<tr>
<td>Isothermal</td>
<td>0</td>
<td>$-W$</td>
<td>$-nRT \ln(V_f/V_i)$</td>
</tr>
<tr>
<td>General</td>
<td>$nc'_v\Delta T$</td>
<td>$\Delta E_{int}-W$</td>
<td>(PV area)</td>
</tr>
</tbody>
</table>
Adiabatic Process ONLY

\[ \Delta E_{\text{int}} = Q_{\text{in}} + W_{\text{on}} \]

\[ n c'_v dT = C_v \, dT = 0 + (-PdV) \]

\[ C_v \, dT = -nRT \, dV/V \]

\[ \frac{dT}{T} = -\frac{nR}{C_v} \frac{dV}{V} \]

\[
-\alpha \int \frac{dV}{V} = -\alpha \ln(V) + C = \ln(V^{-\alpha}) + C = \ln \left( \frac{1}{V^{\alpha}} \right) + C
\]

\[
\ln(T) - \ln \left( \frac{1}{V^{\alpha}} \right) = \ln \left[ \frac{T}{1/V^\alpha} \right] = \ln \left[ TV^{\alpha} \right] = C
\]

\[ \therefore \ln \left( TV^{nR/C_v} \right) = \text{constant} \]

**Key Idea:** the quantity on the left is constant during an adiabatic process involving an ideal gas!
Rewrite:

\[ \frac{nR}{C_V} = \frac{C_p}{C_V} = \gamma - 1 \]

\[ \gamma \equiv \frac{C_p}{C_V} \]

\[ TV \ gamma^{-1} = \text{constant} \]  \hspace{1cm} \text{if } T,V \text{ are known}

rewrite, using the ideal gas law:

\[ \frac{PV}{nR} \ \gamma^{-1} = \text{constant} \]

if the number of moles is constant during the process, then

\[ PV \ \gamma = \text{some other constant} \]  \hspace{1cm} \text{if } P,V \text{ are known}
Adiabatic Compression

\[ PV^\gamma = \text{constant} \]

<table>
<thead>
<tr>
<th></th>
<th>Monatomic gas</th>
<th>Diatomic gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>( 5/3 \approx 1.667 )</td>
<td>( 7/5 = 1.400 )</td>
</tr>
</tbody>
</table>
Calculating the Work in an Adiabatic Compression

\[ \begin{align*}
    dE_{\text{int}} &= dQ_{\text{in}} + dW_{\text{on}}^0 \\
    dW_{\text{on}} &= dE_{\text{int}} - dQ_{\text{in}} \\
    dW_{\text{adiabatic}} &= dE_{\text{int}} = C_v dT \\
    W_{\text{adiabatic}} &= C_v \int_{T_i}^{T_f} dT = C_v \left( T_f - T_i \right) \quad \text{only depends on } \Delta T !
\end{align*} \]

using \( PV = nRT \Rightarrow T = \frac{PV}{nR} \)

\[ W_{\text{adiabatic}} = C_v \left[ \frac{P_f V_f}{nR} - \frac{P_i V_i}{nR} \right] \]

\[ = \left( \frac{P_f V_f - P_i V_i}{\gamma - 1} \right) \quad \text{since } \frac{nR}{C_v} = \gamma - 1 \]
Example:
If 1 mole of an ideal diatomic gas, initially at 310 K, expands adiabatically from 12 L to 19 L, what is the final temperature?

\[ TV \; \gamma^{-1} = \text{constant} \]

For diatomic gas, \( C_V = 5/2 \; R \)

For diatomic gas, \( C_P = 7/2 \; R \)

\[ \gamma \equiv \frac{C_P}{C_V} = 1.4000 \; \text{for diatomic gas} \]

\[ T_i V_i \; \gamma^{-1} = T_f V_f \; \gamma^{-1} \]

Solving for \( T_f \) gives 258 K
Example:
30 moles of a monatomic ideal gas at 1 atmosphere pressure expands adiabatically from an initial volume of 1.5 m³ to 3.0 m³.

\[ PV^\gamma = \text{constant} \]

\[ P, V \]

a. What is the final pressure?

\[ \gamma = \frac{C_P}{C_V} = 1.667 \] (Note this is an approximation to \([5/3]\))

constant = \( P_i \ V_i^\gamma = 1.99 \times 10^5 \ \text{Pa m}^5 \)

\( P_f \ V_f^\gamma = 1.99 \times 10^5 \ \text{Pa m}^5 \)

\[ P_f = 3.19 \times 10^4 \ \text{Pa} \rightarrow T_f = \frac{P_fV_f}{nR} = 383 \ \text{K} \]

\[ P_i = 1.01 \times 10^5 \ \text{Pa} \rightarrow T_i = 607 \ \text{K} \]
b. What is the work done on the gas?

\[ W_{on} = -\int PdV \quad \text{Note that } P \text{ must be inside the integral!} \]

\[ PV^\gamma = \text{constant } \equiv C = 1.99 \times 10^5 \]

\[ W_{on} = -C \int \frac{dV}{V^\gamma} = -C \left. \frac{V^{-\gamma+1}}{-\gamma+1} \right|_V^V_f \]

\[ \gamma = 1.667 \quad 1 - \gamma = -0.667 \quad \Rightarrow \quad \frac{1}{-\gamma+1} = -\frac{3}{2} \]

\[ W_{on} = -C \left[ -\frac{3}{2} \right] \left[ V_f^{-0.667} - V_i^{-0.667} \right] \]

\[ = \frac{3C}{2} \left[ 0.4807 - 0.7631 \right] = -\frac{3C}{2} (0.2824) \]

\[ = -84,350J = -84.4kJ \]

(also equals change in internal energy)
The work can also be calculated from

\[ W_{\text{adiabatic}} = \frac{P_f V_f - P_i V_i}{\gamma - 1} \]

\[ = \left[ \frac{3.19 \times 10^4 \times 3 - 1.013 \times 10^5 \times 1.5}{1.667 - 1} \right] \]

\[ = -84,375 \text{ J} \]

C. Is TV^{\gamma-1} really a constant?

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

\[ 607 \cdot (1.5)^{0.667} = 383 \cdot (3)^{0.667} \]

\[ 607 \cdot 1.310 = 383 \cdot 2.080 \]

\[ 795.2 \approx 796.7 \]

To do better, use 2/3=0.6666666667 instead of 0.667 throughout the calculation.
In summary, for the process under consideration, we have:

\[ PV \gamma = \text{constant} \]

Area under curve \( \approx 84,375 \text{ J} \)