Heat Capacity

Theory and measurement of heat capacity ratio, $\gamma$
Definition and units

**Heat capacity** is the measurable physical quantity that characterizes the amount of heat required to change a substance's temperature by a given amount.

**Units:** In the International System of Units (SI), heat capacity is expressed in units of joule (J) per Kelvin (K). 

\[ \text{[J} \times \text{K}^{-1} \]\n
**Specific heat capacity** is the heat capacity per unit mass of a material.

**Units:** specific heat capacity is expressed in units of joule (J) per kilogram (kg) × Kelvin (K). 

\[ \text{[J} \times \text{kg}^{-1} \times \text{K}^{-1} \]\n
In chemistry, heat capacity is often specified relative to one mole and is called the **molar heat capacity**.

**Units:** molar heat capacity is expressed in units of joule (J) per mol (mol) × Kelvin (K). 

\[ \text{[J} \times \text{mol}^{-1} \times \text{K}^{-1} \]
Thermodynamic definition
Heat capacity at constant volume

The internal energy $dU$ of a closed system changes either by adding or removing heat $dQ$ to the system, or by the system performing work $dW$ or having work done on it.

$$dU = dQ - dW$$

For work as a result of compression or expansion of the system volume $dV$:

$$dU = dQ - PdV$$

If the process is performed at constant volume, then the second term of this relation vanishes and one readily obtains

$$\left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial Q}{\partial T} \right)_V = C_V$$

$C_V$ is the heat capacity at constant volume.
Thermodynamic definition
Heat capacity at constant pressure

The enthality $H$ of the system is given by

$$dH = dU + d(PV)$$

Using $dU = dQ - PdV$ it can be simplified to

$$dH = dQ + VdP$$

At constant pressure we have

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

$C_P$ is the **heat capacity at constant pressure**.
Heat Capacity Ratio $\gamma$

By the definition:

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

Using the thermodynamics one can show, that for ideal gas

$$C_P - C_V = R$$

Or

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

Where $R = 8.31447 \text{ J} \times \text{K}^{-1} \times \text{mole}^{-1}$ is the universal gas constant
Equipartition Theorem

The Equipartition Theorem states that energy is shared equally among all energetically accessible degrees of freedom of a system.

Degree of Freedom is the minimum number of coordinates required to specify the position of a particle or system of particles

1 atom: 3 degrees of freedom (x, y, z)
2 atoms: \(3 \times 2 = 6\) degrees of freedom \((x_1, y_1, z_1, x_2, y_2, z_2)\)
\(N\) atoms: \(3 \times N\) degrees of freedom \((x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)\)

Equipartition Theorem states that each quadratic degree of freedom will possess an energy \(\frac{1}{2}k_bT\), or \(\frac{1}{2}RT\) per mole.

where \(k_b = 1.38065 \times 10^{-23} \text{ J} \times \text{K}^{-1}\) is Boltzmann’s constant
\(R = 8.31447 \text{ J} \times \text{K}^{-1} \times \text{mole}^{-1}\) is Universal gas constant

A quadratic degree of freedom is one for which the energy depends on the square of some property (for instance, velocity \(v\) or angular velocity \(\omega\)).
Equipartition Theorem

Consider the kinetic and potential energies associated with *translational*, *rotational* and *vibrational* energy.

Instead of keeping an eye on the each atom, one can watch

i) translation of center of mass of the system
ii) rotation of the system (change of the orientation in space)
iii) vibration of the system (displacement of the atoms from their equilibrium)

Number of Degrees of Freedom $DF_s$ of system with $N$ atoms

$$DF_s = DF_{\text{trans}} + DF_{\text{rot}} + DF_{\text{vib}} = 3N$$

Internal energy $U$ of system

$$U = \langle E_{\text{trans}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}} \rangle$$

$$\langle E_{\text{vib}} \rangle = \langle E_{\text{vib}_\text{kin}} \rangle + \langle E_{\text{vib}_\text{pot}} \rangle$$

$$U = \langle E_{\text{trans}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}_\text{kin}} \rangle + \langle E_{\text{vib}_\text{pot}} \rangle$$
Equipartition Theorem

Monatomic gases

Ideal monatomic gas has only translation degree of freedom

\[ U = E_{\text{trans}} \]

Internal energy can be expressed as

\[ \langle E_{\text{trans}} \rangle = \frac{1}{2} m \langle v_x \rangle^2 + \frac{1}{2} m \langle v_y \rangle^2 + \frac{1}{2} m \langle v_z \rangle^2 \]

Or, according to equipartition theorem, per 1 mole:

\[ \langle E_{\text{trans}} \rangle = \frac{1}{2} RT + \frac{1}{2} RT + \frac{1}{2} RT = \frac{3}{2} RT \quad \text{(number of degrees of freedom times RT/2)} \]

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v = \left( \frac{\partial \langle E_{\text{trans}} \rangle}{\partial T} \right)_v = \frac{\partial}{\partial T} \left( \frac{3}{2} RT \right)_v = \frac{3}{2} R \]

\[ C_p = C_v + R = \frac{5}{2} R \quad \Rightarrow \quad \gamma \equiv \frac{C_p}{C_v} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = \frac{5}{3} \]

For ideal monatomic gas

\[ \gamma \approx 1.67 \]
Equipartition Theorem

Diatomic gases

Internal energy of the system

$$U = \langle E_{\text{trans}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib\_kin}} \rangle + \langle E_{\text{vib\_pot}} \rangle$$

$$\langle E_{\text{trans}} \rangle = \frac{1}{2} \mu \langle v_{\mu}^2 \rangle;$$

$$\langle E_{\text{rot}} \rangle = \frac{1}{2} I \langle \omega^2 \rangle$$

$$\langle E_{\text{vib\_kin}} \rangle = \frac{1}{2} \mu \langle v_{12}^2 \rangle;$$

$$\langle E_{\text{vib\_pot}} \rangle = \frac{1}{2} k r_0^2$$

$$U = 3 \times \frac{1}{2} RT + 2 \times \frac{1}{2} RT + 1 \times \frac{1}{2} RT + 1 \times \frac{1}{2} RT = \frac{7}{2} RT$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{7}{2} RT \right)_V = \frac{7}{2} R$$

$$C_P = C_V + R = \frac{9}{2} R \quad \Rightarrow \quad \gamma = \frac{C_P}{C_V} = \frac{9}{7}$$

For ideal diatomic gas

$$\gamma = \frac{9}{7} \approx 1.29$$
Equipartition Theorem

Polyatomic gases

Calculation of vibrational degrees of freedom for triatomic molecules

\[ DF_{vibrational} = DF_s - DF_{translation} - DF_{rotational} \]

**Linear molecule:** CO\(_2\); \(N = 3\) \(\Rightarrow\) \(DF_s = 9\); \(DF_{translation} = 3\); \(DF_{rotational} = 2\)

\(DF_{vibrational} = 9 - 3 - 2 = 4\)

\[ U = \left(3 + 2 + 4 \times 2\right) \frac{1}{2} RT = \frac{13}{2} RT; \quad C_v = \frac{13}{2} R; \quad C_p = \frac{15}{2} R; \quad \gamma \approx 1.15 \]

\[ \begin{array}{c}
\text{Symmetric stretch} \\
\text{Asymmetric stretch} \\
\text{Bending(1)} \\
\text{Bending(2)}
\end{array} \]

**Nonlinear molecule:** H\(_2\)O; \(N = 3\) \(\Rightarrow\) \(DF_s = 9\); \(DF_{translation} = 3\); \(DF_{rotational} = 3\) \(DF_{vibrational} = 3\)

\[ U = \left(3 + 3 + 3 \times 2\right) \frac{1}{2} RT = \frac{12}{2} RT; \]

\[ C_v = \frac{12}{2} R; \quad C_p = \frac{14}{2} R; \quad \gamma \approx 1.17 \]
Adiabatic expansion

1. Fill the carboy with the N\textsubscript{2} gas ($P_1 > P_2 = P_{\text{atm}}$)
2. Wait to reach the $T_1 = T_{\text{room}}$ (explain, why)
3. Measure the pressure $P_1$ (initial pressure)
4. Release the gas by removing the stopper
5. Wait to reach the $T_3 = T_{\text{room}}$ (explain, why)
6. Measure the pressure $P_3$ (final pressure)
7. Repeat the measurements 3 times

Experimental setup

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Adiabatic expansion

\[ P_1, V_1, T_{\text{room}} \rightarrow P_{\text{atm}}, V_2, T_2 \rightarrow P_3, V_2, T_{\text{room}} \]

\[ PV = nRT \quad dU = dQ - PdV = -PdV = -nRT \frac{dV}{V} \]

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v \Rightarrow dU = C_v dT = -nRT \frac{dV}{V} \Rightarrow C_v \frac{dT}{T} = -R \frac{dV}{V} \quad \text{(for 1 mole)} \]

\[ C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad \Rightarrow \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} \]

\[ \ln \frac{P_2}{P_1} = -C_p \ln \left( \frac{V_2}{V_1} \right) \]

\[ P_1 V_1 = P_3 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_3} \]

\[ \gamma \equiv \frac{C_p}{C_v} = \frac{\ln \left( \frac{P_1}{P_2} \right)}{\ln \left( \frac{V_2}{V_1} \right)} \]

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Adiabatic expansion

References


Sound Velocity Method

Sound Velocity $v_S$ can be expressed as:

$$V_S = \left(\frac{\gamma RT}{M}\right)^{1/2}$$

Where:

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

- $R$ – universal gas constant
- $T$ – temperature
- $M$ – molecular weight

If we know the speed of sound, we can calculate $\gamma$
Sound Velocity Method

What the sound is?

Definition of sound:

Vibrations transmitted through an elastic solid or a liquid or gas, with frequencies in the approximate range of 20 Hz to 20 kHz

Characteristics of sound:

\[ f \] – frequency [number of vibrations per unit of time, Hz, or s\(^{-1}\)]

\[ \lambda \] – wavelength [m]

By definition \[ \lambda = \frac{v_S}{f} \] \[ \iff \] Speed of sound can be found as \[ v_S = \lambda f \]

So, our goal is to measure the wavelength and the frequency of the sound
Sound Velocity Method

Experimental Setup

- Generator
- Speaker
- Gas in
- Gas out
- Microphone
- Movable rod
- Kundt’s tube
- To oscilloscope

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If the Generator output is connected to Y1 input of the Scope and the Microphone output is connected to Y2 input, the Scope shows 2 similar sin waveforms.
If the Generator output is connected to Y1 input of the Scope and the Microphone output is connected to X input, the Scope shows so called *Lissajous pattern*.

A Lissajous pattern is a graph of one frequency plotted on the y axis combined with a second frequency plotted on the x axis. In our case both \( f \) are the same.
Sound Velocity Method

Mathematical description of the simplest Lissajous pattern

Scope shows $y$ as a function of $x$

$$y = y(x)$$

We know the time dependence both $y$ and $x$

$$y(t) = Y_0 \sin(ft)$$

$$x(t) = X_0 \sin(ft - \Delta \varphi)$$

Where $\Delta \varphi$ is the phase difference between $y(t)$ and $x(t)$

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Mathematical description of the simplest Lissajous pattern

\[ y(t) = Y_0 \sin(ft) \]
\[ x(t) = X_0 \sin(ft - \Delta \varphi) \]

Assuming \( X_0 = Y_0 \)

If \( \Delta \varphi = 0 \)

\[ y(t) = \sin(ft) \]
\[ x(t) = \sin(ft) \]

\[ y^2(t) + x^2(t) = \sin^2(ft) + \cos^2(ft) = 1 \]

If \( \Delta \varphi = \pi/2 \) (a quarter of period)

\[ y(t) = \sin(ft) \]
\[ x(t) = \sin(ft - \pi/2) = \cos(ft) \]

\[ y^2(t) + x^2(t) = 1 \]
Mathematical description of the simplest Lissajous pattern

\[ y(t) = Y_0 \sin(ft) \]
\[ x(t) = X_0 \sin(ft - \Delta\varphi) \]

Assuming \( X_0 = Y_0 \)

If \( \Delta\varphi = \pi \)

(a half of period)

\[ y(t) = \sin(ft) \]
\[ x(t) = \sin(ft - \pi) = -\sin(ft) \]

\[ y^2(t) + x^2(t) = \sin^2(ft) + \cos^2(ft) = 1 \]

If \( \Delta\varphi = \frac{3\pi}{2} \)

(three quarters of period)

\[ y(t) = \sin(ft) \]
\[ x(t) = \sin(ft - \frac{3\pi}{2}) = -\cos(ft) \]

\[ y^2(t) + x^2(t) = 1 \]

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Mathematical description of the simplest Lissajous pattern

\[ y(t) = Y_0 \sin(ft) \]
\[ x(t) = X_0 \sin(ft - \Delta \varphi) \]

Assuming \( X_0 = Y_0 \)

\[ y(t) = \sin(ft) \]
\[ x(t) = \sin(ft) \]

If \( \Delta \varphi = 2\pi \)
(full period)

Full period corresponds to \( \lambda \)

<table>
<thead>
<tr>
<th>Phase difference</th>
<th>0</th>
<th>a quarter of period, or ( \lambda/4 )</th>
<th>a half of period, or ( \lambda/2 )</th>
<th>three quarters of period, or ( 3\lambda/4 )</th>
<th>full period, or ( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure on the scope</td>
<td>( / )</td>
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</tr>
</tbody>
</table>

Note: if \( X_0 \neq Y_0 \) the angle will be not 45\(^0\) and the circles become the ellipses
How to measure the wavelength?

Frequency is given by generator

Generator

Scope

X

Y

Microphone

Speaker

λ

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How to measure the wavelength?

Frequency is given by generator

Speaker $\lambda$

Generator

$\frac{\lambda}{4}$

Microphone

Scope $Y$

$X$

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How to measure the wavelength?

Frequency is given by generator

Speaker

\[ \lambda \]

\[ \frac{\lambda}{2} \]

Generator

Microphone

Scope

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How to measure the wavelength?

Frequency is given by generator

Speaker

Generator

Scope

Microphone

$\lambda$

$\frac{3\lambda}{4}$
How to measure the wavelength?

Frequency is given by generator

Generator

Scope

Microphone

Speaker

How to measure the wavelength?

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Experiment

1. Measure the shape of Lissajous pattern as a function of microphone position

2. Distance between two positions corresponding to straight $45^0$ line is equal to the wavelength of the sound in given gas at given sound frequency

3. Calculate the speed of sound in given gas at given frequency using formula

$$v_S = \lambda f$$
Sound Velocity Method

References

