Announcements

1. Please bring your laptops to lab this week.

2. Physics seminar this week – Thursday, Nov. 20 at 4 PM – Professor Brian Matthews will discuss relationships between protein structure and function

3. Schedule –

   Today, Nov. 18th: Examine $E_{\text{int}}$ especially for ideal gases

   Discuss ideal gas law

   Continue discussion of first law of thermodynamics

   Thursday, Nov. 20th: Review Chapters 15-20

   Tuesday, Nov. 25th: Third exam
From The New Yorker Magazine, November 2003

"Quick, get it while its molecules are still vibrating."
First law of thermodynamics

\[ \Delta E_{\text{int}} = Q - W \]

\[ W = \int_{V_i}^{V_f} PdV \]

For an “ideal gas” we can write an explicit relation for \( E_{\text{int}} \).

What we will show:

\[ E_{\text{int}}^{(\text{ideal gas})} = \frac{n}{\gamma - 1} RT = \frac{N}{\gamma - 1} k_B T \]

\( \gamma \) is a parameter which depends on the type of gas (monoatomic, diatomic, etc.) which can be measured as the ratio of two heat capacities: \( \gamma = C_P / C_V \).
Thermodynamic statement of conservation of energy –

First Law of Thermodynamics

\[ \Delta E_{\text{int}} = Q - W \]

- Heat added to system \( Q \) \textit{if} \ depends on path
- Work done by system \( W \) \textit{if} \ depends on path
- “Internal” energy of system

\[ \Delta E_{\text{int}} = E_{\text{int}(f)} - E_{\text{int}(i)} \rightarrow \text{independent on path} \]
How is temperature related to $E_{\text{int}}$?

Consider an ideal gas

- Analytic expressions for physical variables
- Approximates several real situations

Ideal Gas Law: $P \ V = n \ R \ T$

- Pressure (Pa)
- Volume ($m^3$)
- Number of moles
- Temperature (K)
- Gas constant ($8.31 \text{ J/(mole} \cdot \text{K)}$)
Ideal gas – P-V diagram at constant $T$

$$PV = nRT$$

![Diagram showing P-V relationship for ideal gas at different temperatures.](image)
The diagram above shows a process in which one mole of an ideal gas expands and contracts between volumes $V_1 = 1\text{m}^3$ and $V_2 = 2\text{m}^3$ pressures $P_1 = 101300\text{ Pa}$ and $P_2 = 202600\text{ Pa}$.

1. At what point does the system have the highest temperature? (a) A (b) B (c) C (d) D
2. For which steps does the system do positive work? (a) A->B (b) B->C (c) C->D (d) D->A
3. For which steps does the system do negative work? (a) A->B (b) B->C (c) C->D (d) D->A
4. For which steps does the system do no work? (a) A->B (b) B->C (c) C->D (d) D->A
Microscopic model of ideal gas:

Each atom is represented as a tiny hard sphere of mass $m$ with velocity $v$. Collisions and forces between atoms are neglected. Collisions with the walls of the container are assumed to be elastic.
What we can show is the pressure exerted by the atoms by their collisions with the walls of the container is given by:

\[ P = \frac{2}{3} \frac{N}{V} \frac{1}{2} m \left\langle v^2 \right\rangle_{\text{avg}} = \frac{2}{3} \frac{N}{V} \left\langle K \right\rangle_{\text{avg}} \]

Proof:

Force exerted on wall perpendicular to x-axis by an atom which collides with it:

\[ F_{ix} = -\frac{\Delta p_{ix}}{\Delta t} = \frac{2m_i v_{ix}}{\Delta t} \quad \Delta t \approx 2d / v_{ix} \]

\[ \Rightarrow F_{ix} \approx \frac{2m_i v_{ix}^2}{2d / v_{ix}} = \frac{m_i v_{ix}^2}{d} \]

\[ P = \sum_i \frac{F_{ix}}{A} = \sum_i \frac{m_i v_{ix}^2}{dA} = \frac{N}{V} \left\langle m_i v_{ix}^2 \right\rangle \rightarrow \text{average over atoms} \]
Ideal gas law continued:

Recall that

Macroscopic relation: \( PV = nRT = N \frac{R}{N_A} T = Nk_B T \)

Microscopic model: \( PV = \frac{2}{3} N \left\{ \frac{1}{2} m \langle v^2 \rangle \right\} = Nk_B T \)

Therefore:

\[
\left\{ \frac{1}{2} m \langle v^2 \rangle \right\} = \frac{3}{2} k_B T
\]

\[\Rightarrow \nu_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}\]

Also:

\[
\left\{ \frac{1}{2} m \langle v^2 \rangle \right\} = \frac{3}{2} k_B T
\]

\[\Rightarrow E_{int} = N \left\{ \frac{1}{2} m \langle v^2 \rangle \right\} = N \frac{3}{2} k_B T\]
Internal energy of an ideal gas:

\[ E_{\text{int}} = N \left\{ \frac{1}{2} m \langle v^2 \rangle \right\} = N \frac{3}{2} k_B T \Rightarrow \frac{N}{\gamma - 1} k_B T = \frac{n}{\gamma - 1} RT \]

derived for monoatomic ideal gas

more general relation for polyatomic ideal gas

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \gamma ) (theory)</th>
<th>( \gamma ) (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>5/3</td>
<td>1.67</td>
</tr>
<tr>
<td>N(_2)</td>
<td>7/5</td>
<td>1.41</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>4/3</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Big leap!
Determination of $Q$ for various processes in an ideal gas:

$$E_{\text{int}} = \frac{n}{\gamma-1} RT$$

$$\Delta E_{\text{int}} = \frac{n}{\gamma-1} R \Delta T = Q - W$$

Example: Isovolumetric process – \(V=\text{constant} \Rightarrow W=0\)

$$\Delta E_{\text{int}_{i\rightarrow f}} = \frac{n}{\gamma-1} R \Delta T_{i\rightarrow f} = Q_{i\rightarrow f}$$

In terms of “heat capacity”:

$$Q_{i\rightarrow f} = \frac{n}{\gamma-1} R \Delta T_{i\rightarrow f} \equiv nC_V \Delta T_{i\rightarrow f}$$

$$C_V = \frac{R}{\gamma-1}$$
Example: Isobaric process (P=constant):

\[ \Delta E_{\text{int}i\rightarrow f} = \frac{n}{\gamma-1} R\Delta T_{i\rightarrow f} = Q_{i\rightarrow f} - W_{i\rightarrow f} \]

In terms of “heat capacity”:

\[ Q_{i\rightarrow f} = \frac{n}{\gamma-1} R\Delta T_{i\rightarrow f} + P_i(V_f-V_i) = \frac{n}{\gamma-1} R\Delta T_{i\rightarrow f} + nR\Delta T_{i\rightarrow f} \equiv nC_p\Delta T_{i\rightarrow f} \]

\[ \Rightarrow C_p = \frac{R}{\gamma-1} + R = \frac{\gamma R}{\gamma-1} \]

Note: \( \gamma = \frac{C_p}{C_V} \)
More examples:

Isothermal process \((T=0)\)

\[
E_{\text{int}} = \frac{n}{\gamma - 1} RT
\]

\[
\Delta E_{\text{int}} = \frac{n}{\gamma - 1} R \Delta T = Q - W
\]

\[\Rightarrow \Delta T = 0 \quad \Rightarrow \Delta E_{\text{int}} = 0 \quad \Rightarrow Q = W\]

\[
W = \int_{V_i}^{V_f} P \, dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln \left( \frac{V_f}{V_i} \right)
\]
Even more examples:

Adiabatic process (Q=0)

\[ \Delta E_{\text{int}} = -W \]

\[ \frac{n}{\gamma - 1} R\Delta T = -P\Delta V \]

\[ PV = nRT \]

\[ \Delta PV + P\Delta V = nR\Delta T \]

\[ nR\Delta T = -(\gamma - 1)P\Delta V = \Delta PV + P\Delta V \]

\[ -\gamma \frac{\Delta V}{V} = \frac{\Delta P}{P} \]

\[ \Rightarrow -\ln\left(\frac{V_f^\gamma}{V_i^\gamma}\right) = \ln\left(\frac{P_f}{P_i}\right) \Rightarrow P_i V_i^\gamma = P_f V_f^\gamma \]
Adiabat: \[ P = \frac{P V_i^\gamma}{V^\gamma} \]

Isotherm: \[ P = \frac{P V_i}{V} \]
Peer instruction question

Suppose that an ideal gas expands adiabatically. Does the temperature

(A) Increase     (B) Decrease      (C) Remain the same

\[ P_i V_i^\gamma = P_f V_f^\gamma \]

\[ P_i V_i = nRT_i \Rightarrow P_i = nR \frac{T_i}{V_i} \]

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

\[ T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma-1} \]
Review of results from ideal gas analysis in terms of the specific heat ratio $\gamma \equiv C_p/C_V$:

$$\Delta E_{\text{int}} = \frac{n}{\gamma-1} R\Delta T = nC_V\Delta T \quad ; \quad C_V = \frac{R}{\gamma-1}$$

$$C_P = \frac{\gamma R}{\gamma-1}$$

For an isothermal process, $\Delta E_{\text{int}} = 0 \rightarrow Q=W$

$$W = \int_{V_i}^{V_f} PdV = nRT \ln \left( \frac{V_f}{V_i} \right) = P_iV_i \ln \left( \frac{V_f}{V_i} \right)$$

For an adiabatic process, $Q = 0$

$$P_iV_i^\gamma = P_fV_f^\gamma$$

$$T_iV_i^{\gamma-1} = T_fV_f^{\gamma-1}$$
Extra credit:

Show that the work done by an ideal gas which has an initial pressure $P_i$ and initial volume $V_i$ when it expands *adiabatically* to a volume $V_f$ is given by:

$$W = \int_{V_i}^{V_f} PdV = \frac{P_i V_i}{\gamma - 1} \left( 1 - \left( \frac{V_i}{V_f} \right)^{\gamma - 1} \right)$$
Peer instruction questions

Match the following types of processes of an ideal gas with their corresponding P-V relationships, assuming the initial pressures and volumes are $P_i$ and $V_i$, respectively.

1. Isothermal
2. Isovolumetric
3. Isobaric
4. Adiabatic

(A) $P=P_i$ (B) $V=V_i$ (C) $PV=P_i V_i$ (D) $PV^\gamma=P_i V_i^\gamma$
Examples process by an ideal gas:

\[ P_f (V_f - V_i) \gamma \frac{1}{\gamma - 1} \]

\[ \Delta E_{int} = \frac{V_f (P_f - P_i)}{\gamma - 1} \]

\[ W = P_f (V_f - V_i) \]

\[ Q = V_i (P_f - P_i) \gamma \frac{1}{\gamma - 1} \]

\[ e = \frac{W_{net}}{Q_{input}} \]
5. One mole of an ideal monatomic gas traverses the cycle of Fig. 20-24. Process 1-->2 occurs at constant volume, process 2-->3 is adiabatic, and process 3-->1 occurs at constant pressure.

![Diagram of a cycle with points labeled 1, 2, and 3, pressures T_2 = 600 K, T_1 = 300 K, and T_3 = 455 K. The cycle is labeled as adiabatic.]

(a) Compute the heat Q, the change in internal energy ΔE_{int}, and the work done W, for each of the three processes and for the cycle as a whole.

For 1-->2: \( Q = [0.0769231] \) J, \( ΔE_{int} = [0.0769231] \) J, \( W = [0.0769231] \) J

For 2-->3: \( Q = [0.0769231] \) J, \( ΔE_{int} = [0.0769231] \) J, \( W = [0.0769231] \) J

For 3-->1: \( Q = [0.0769231] \) J, \( ΔE_{int} = [0.0769231] \) J, \( W = [0.0769231] \) J

For cycle: \( Q = [0.0769231] \) J, \( ΔE_{int} = [0.0769231] \) J, \( W = [0.0769231] \) J

(b) The initial pressure at point 1 is 1.00 atm. Find the pressure and the volume at points 2 and 3. Use 1.00 atm=1.013 x 10^{-5} Pa and \( R = 8.314 \) J/molK.

At point 2: \( P = [0.0769231] \) Pa, \( V = [0.0769231] \) m³

At point 3: \( P = [0.0769231] \) Pa, \( V = [0.0769231] \) m³