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_{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



First law of thermodynamics

$$\Delta E_{int} = Q - W$$

$$W = \int\limits_{V_i}^{V_f} P dV$$

For an "ideal gas" we can write an explicit relation for E_{int} .

What we will show:

$$E_{\text{int}}^{(\text{ideal gas})} = \frac{n}{\gamma - 1}RT = \frac{N}{\gamma - 1}k_BT$$

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

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Thermodynamic statement of conservation of energy -

First Law of Thermodynamics



How is temperature related to E_{int} ?

Consider an ideal gas

- → Analytic expressions for physical variables
- → Approximates several real situations

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

volume (m³)
pressure (Pa)
temperature (K)
gas constant (8.31 J/(mole ·K))
number of moles

Ideal gas – P-V diagram at constant T





The diagram above shows a process in which one mole of an ideal gas expands and contracts between volumes $V_1 = 1m^3$ and $V_2 = 2m^3$ pressures $P_1 = 101300$ Pa and $P_2 = 202600$ 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

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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.





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What we can show is the pressure exerted by the atoms by their collisions with the walls of the container is given by:

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

Proof:

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

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

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

$$P = \sum_i \frac{F_{ix}}{A} = \sum_i \frac{m_i v_{ix}^2}{dA} = \frac{N}{V} \langle m_i v_x^2 \rangle \qquad d$$
number of atoms
$$P = \sum_i \frac{F_{ix}}{A} = \sum_i \frac{m_i v_{ix}^2}{dA} = \frac{N}{V} \langle m_i v_x^2 \rangle \qquad d$$
average over atoms
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Ideal gas law continued:

Recall that Macroscopic relation : $PV = nRT = N\frac{R}{N_A}T = Nk_BT$ Microscopic model: $PV = \frac{2}{3}N\left\{\frac{1}{2}m\langle v^2\rangle\right\} = Nk_BT$ Therefore: $\left\{\frac{1}{2}m\langle v^2 \rangle\right\} = \frac{3}{2}k_BT$ $\Rightarrow v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$ Also: $\left\{\frac{1}{2}m\langle v^2 \rangle\right\} = \frac{3}{2}k_BT$ $\Rightarrow E_{\text{int}} = N \left\{ \frac{1}{2} m \left\langle v^2 \right\rangle \right\} = N \frac{3}{2} k_B T$

Big leap!
Internal energy of an ideal gas:

$$E_{int} = N\left\{\frac{1}{2}m\langle v^2 \rangle\right\} = N\frac{3}{2}k_BT \Rightarrow \frac{N}{\gamma-1}k_BT = \frac{n}{\gamma-1}RT$$
derived for monoatomic
ideal gas
more general relation for
polyatomic ideal gas

Gas	γ (theory)	γ (exp)
Не	5/3	1.67
N ₂	7/5	1.41
H ₂ O	4/3	1.30

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

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Example: Isobaric process (P=constant):

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

In terms of "heat capacity":

$$Q_{i \to f} = \frac{n}{\gamma - 1} R \Delta T_{i \to f} + P_i \left(V_f - V_i \right) = \frac{n}{\gamma - 1} R \Delta T_{i \to f} + n R \Delta T_{i \to f} \equiv n C_p \Delta T_{i \to f}$$
$$\implies C_p = \frac{R}{\gamma - 1} + R = \frac{\gamma R}{\gamma - 1}$$

Note:
$$\gamma = C_P / C_V$$

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More examples:

Isothermal process (T=0)

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

$$\Delta T = 0 \quad \Rightarrow \Delta E_{int} = 0 \quad \Rightarrow Q = W$$

$$W = \int_{V_i}^{V_f} P dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right)$$

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Even more examples:

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Adiabatic process (Q=0)
          \Delta E_{\rm 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) \quad \Rightarrow P_i V_i^{\gamma} = P_f V_f^{\gamma}
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Peer instruction question

Suppose that an ideal gas expands adiabatically. Does the temperature

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

$$\begin{split} P_i V_i^{\gamma} &= P_f V_f^{\gamma} \\ P_i V_i &= n R T_i \Longrightarrow P_i = n R \frac{T_i}{V_i} \\ T_i V_i^{\gamma - 1} &= T_f V_f^{\gamma - 1} \\ T_f &= T_i \left(\frac{V_i}{V_f} \right)^{\gamma - 1} \end{split}$$

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Review of results from ideal gas analysis in terms of the specific heat ratio $\gamma \equiv C_P/C_V$:

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

For an isothermal process, $\Delta E_{int} = 0 \Rightarrow Q = W$ $W = \int_{V_i}^{V_f} P dV = nRT \ln\left(\frac{V_f}{V_i}\right) = P_i V_i \ln\left(\frac{V_f}{V_i}\right)$ For an adiabatic process, Q = 0 $P_i V_i^{\gamma} = P_f V_f^{\gamma}$ $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

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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:

$$W = \int_{V_i}^{V_f} P dV = \frac{P_i V_i}{\gamma - 1} \left(1 - \left(\frac{V_i}{V_f} \right)^{\gamma - 1} \right)$$

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) $PV=P_iV_i$ (D) $PV^{\gamma}=P_iV_i^{\gamma}$

Examples process by an ideal gas:



5. HRW6 20.P061.NH [306369] 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.



Figure 20-24.

(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]	$J \Delta E_{int} = [0.0769231]$	J W= [0.0769231]	J
For 2>3: Q=[0.0769231]	$J \Delta E_{int} = [0.0769231]$	J W=[0.0769231]	J
For 3>1: Q=[0.0769231]	$J \Delta E_{int} = [0.0769231]$	J W=[0.0769231]	J
For cycle: Q=[0.0769231]	$J \Delta E_{int} = [0.0769231]$	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]	m	3
At point 3: P = [0.0769231]	Pa V = [0.0769231]	m	3

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