

Lecture # 2

1) Energy, Heat, Work, 1st law of thermodynamics

Energy is fundamental concept in all physics, for this reason it cannot be defined through something else. To understand what energy is we should consider examples.

- 1) Energy of translational motion $\frac{1}{2}mv^2$
- 2) Energy of rotation $\frac{1}{2}I\omega^2$
- 3) Energy of vibration $\frac{1}{2}mv^2 + \frac{1}{2}kx^2$
- 4) Potential energy (interaction between bodies)

$$\text{Gravitational } U = -G \frac{m_1 m_2}{r_{12}^2}$$

$$\text{Electrostatic } U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_{12}}$$

- 5) Energy of electromagnetic field in vacuum $U = \frac{E^2}{8\pi} + \frac{H^2}{8\pi}$ (CGS)
- 6) Energy of chemical bond
 $\text{H}^0 + \text{H}^0 \rightarrow \text{H}:\text{H}$ Covalent bond in essence electrostatic
 $\text{Li} + \text{Cl} \rightarrow \text{Li}^+ \text{Cl}^-$ Ionic bond potential energy

7) Nuclear energy – comes from so-called strong interaction between neutrons and protons in atom nuclei.

2) The 1st law of thermodynamics: Energy of closed system is conserved

$$U_T = \sum_{i=1}^N u_i \text{ Total energy.}$$

Examples of energy transformations:

1. Planetary motion



Position 1 – highest kinetic energy, lowest potential energy

Position 2 - highest potential energy, lowest kinetic energy

2. Burning of natural gas (metan)

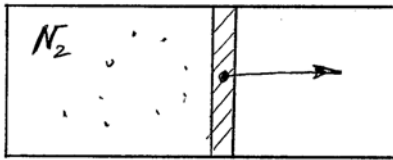
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ + kinetic motion of products (heat) + ionization of molecular (flame) + emission of light (EM radiation energy)

3. Nuclear reaction (chain reaction)

$n + {}_{92}^{235}\text{U} \rightarrow {}_{92}^{236}\text{U} \rightarrow {}_{56}^{144}\text{Ba} + {}_{36}^{89}\text{Kr} + 3n + \underline{177 \text{ MeV}}$. 177 MeV goes into kinetic energy of products, ionization of constitute and EM radiation

- In thermodynamics $U = \sum U$ is often called internal energy of a system. U always has its origin in mechanical motion or some fundamental interaction.

When we consider specific system we often have to take into account one or two energy constitutes and ignore the other because they do not change.



In N_2 expansion we need to take into account for energies related to translational and perhaps rotational and vibrational motion of N_2 but there is no chemical or nuclear transformation so we do not need to account for them in our computations.

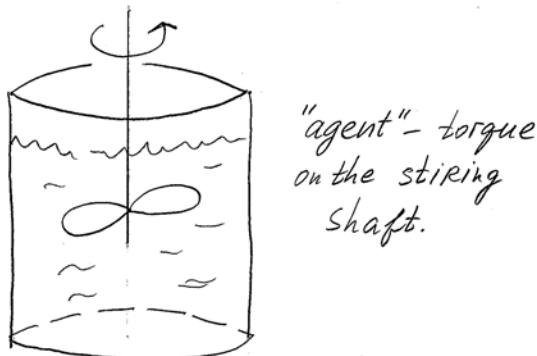
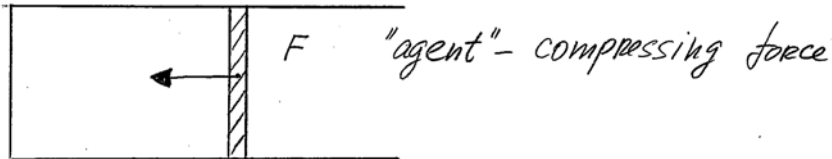
The internal energy of a system can change as a result of exchange between the system and surroundings. There are many mechanism of how it can be done. In thermodynamics we classify these mechanisms under two categories.

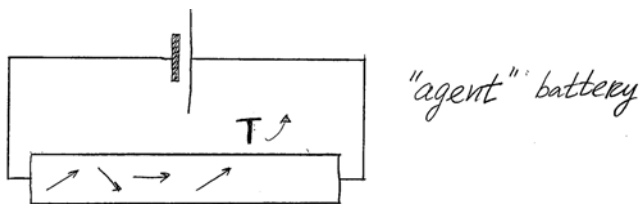
3) HEAT and WORK

Heat is any spontaneous flow of energy from one object to another caused by the difference in temperature. Some mechanisms ---- Conduction, Convection, radiation

Work is any other transfer of energy:

There is always an 'agent' that is actively putting energy into a system or receiving energy from the system.





1st law of thermodynamics – (Law of conservation of energy)

(Our choice, lecture notes) $\Delta U = Q - W_s$ (this course, most of the physical text book)

Q – heat transferred to the system, W_s – work done by the system

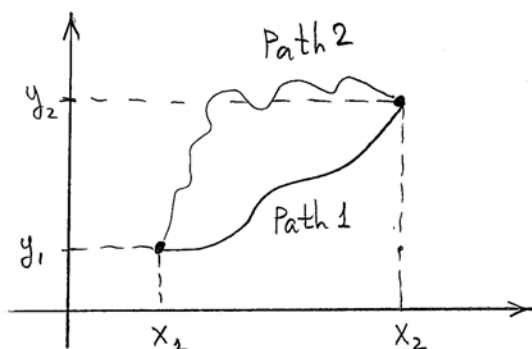
(Schroeder, textbook) $\Delta U = Q + W_{ext}$ (some chemistry books)

W_{ext} – work done on a system by external force.

In practice we need to make a relation between Infinitesimal changes of energy, work and heat. It is tempting to write it in the form.

$$(1) \quad dU = dQ - dW$$

Eq (1) has however a problem from the mathematical stand point. The notation dQ is used to de fine exact differential of the function Q , while in Eq 2.1 neither dQ nor dW are exact differential, that is the integral of $\int_a^b dQ$ depends on path along which this integral is taken.



There is several ways to emphasize this fact.

- 1) Schroeder does not use 'd' sigh at all
- 2) In Illinois textbook one write "d" but 'remember' that this is not an exact differential.
- 3) The most common way that we are going to use in the course is to employ special notations.
 - $dU = dQ - \bar{d}W$ (Kittel, Rief)

The point of notation is to emphasize that $\bar{d}W$ is infinitesimally small number but at the same time is not exact differential. In our course we will use convention (3) but likely sometimes slip into convention (2)

4) Exact and "inexact" differentials

Let us review some related math. Say we have function $f(x, y)$. It is said to have a total (exact) differential at point (x, y) if in the vicinity of (x, y) it can be represented in the form

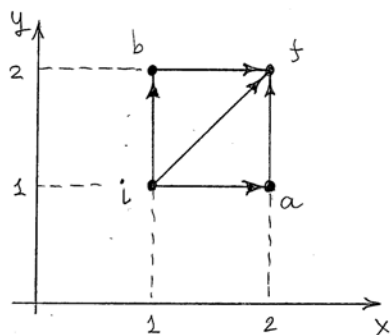
$$f(x + \Delta x, y + \Delta y) - f(x, y) = a\Delta x + b\Delta y + \text{small}(\Delta x^2, \Delta y^2)$$

Where a and b are **independent** of Δx and Δy .

The Linear function $df = a\Delta x + b\Delta y = adx + bdy$ df is termed the total differential.

Let us consider an example

Function: $f(x, y) = a \ln x + b \ln y$. Its differential: $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = \frac{adx}{x} + \frac{bdy}{y}$



We want to show that integration of df along the path $i \rightarrow a \rightarrow f$ gives the same result as integration along the path $i \rightarrow b \rightarrow f$ or $i \rightarrow f$. The path of integration in general is given by parametric equations $x = \varphi(t)$

$y = \psi(t)$.

$$\int_i^f g(x, y)dx + v(x, y)dy = \int_i^f g(\varphi(t), \psi(t)) \varphi'(t)dt + \int_i^f v(\varphi(t), \psi(t)) \psi'(t)dt$$

In our case

| | | |
|-------------------|---------|---------|
| $i \rightarrow a$ | $x = t$ | $y = 1$ |
| $a \rightarrow f$ | $x = 2$ | $y = t$ |
| $i \rightarrow b$ | $x = 1$ | $y = t$ |
| $b \rightarrow f$ | $x = t$ | $y = 2$ |

$i \rightarrow f$?

Along the path $i \rightarrow a \rightarrow f$

$$\int_{i \rightarrow a} \alpha \frac{dx}{x} = \int_{i \rightarrow a} \alpha \frac{dt}{t} = \alpha \ln 2, \quad \int_{a \rightarrow f} \alpha \frac{dx}{x} = \int_{a \rightarrow f} \alpha 0 = 0, \quad \int_{i \rightarrow a} \beta \frac{dy}{y} = 0, \quad \int_{a \rightarrow f} \beta \frac{dy}{y} = \ln 2$$

$$\text{Therefore } \int_{i \rightarrow a \rightarrow f} df = \alpha \ln 2 + \beta \ln 2$$

Along the path $i \rightarrow b \rightarrow f$

$$\int_{i \rightarrow b} \alpha \frac{dx}{x} = 0, \quad \int_{b \rightarrow f} \alpha \frac{dx}{x} = \alpha \ln 2, \quad \int_{i \rightarrow b} \beta \frac{dy}{y} = \beta \ln 2, \quad \int_{b \rightarrow f} \beta \frac{dy}{y} = 0$$

$$\text{Therefore } \int_{i \rightarrow b \rightarrow f} df = \alpha \ln 2 + \beta \ln 2$$

The functions $a = \left(\frac{\partial f}{\partial x} \right)_y$ and $b = \left(\frac{\partial f}{\partial y} \right)_x$ are called partial derivatives of the function f .

Some properties of exact (total) differential

1) In general $a(x, y)$, $b(x, y)$ - are functions of x and y in general

2) If differential exists it is unique.

3) $\int_{x_1, y_1}^{x_2, y_2} df = f(x_2, y_2) - f(x_1, y_1)$ does not depend on path of integration.

Q. direct path integration $i \rightarrow f$

“Inexact” differentials

Nothing prevent us from writing an arbitrary expression for infinitiamally small function, say

$$dg = \alpha dx + \frac{\beta x}{y} dy$$

i-a-f path i-a path : $x=t, y=1$; a-f path: $x=2, y=t$

$$\int_{i \rightarrow a \rightarrow f} dg = \alpha \int_1^2 dt + \int_{i \rightarrow a} [dy=0] + \int_{a \rightarrow f} [dx=0] + \int_1^2 \beta \frac{2}{t} dt = \alpha + 2\beta \ln 2$$

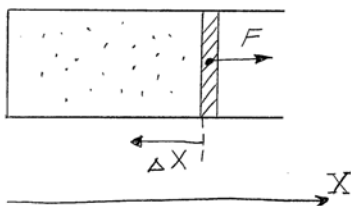
Direct path: $i \rightarrow f$ $x=t, y=t$

$$\int_{i \rightarrow f} dg = \int_1^2 \alpha dt + \int_1^2 \beta \frac{t}{t} dt = \alpha + \beta$$

Conclusion: dg is not total (exact) differential. Integration over different paths gives different values of

$$\int dg$$

4) Compression and expansion work of a gas.



The direction of the force is taken to satisfy our definition “work done by system”.

- We consider quasistatic ‘slow’ process
- Δx is small, total pressure in the system does not change
- The system is thermally isolated no heat flows in or out of the system.

Definition of mechanical work: $W = \vec{F} \cdot \vec{r} = |F||r| \cos \theta$

In our cylinder

(We remove vectors but keep signs, positive for F and negative for Δx .)

$$W = F \Delta x = PS \Delta x = P \Delta V \quad (P - \text{pressure}, S - \text{area of piston})$$

$$1^{\text{st}} \text{ law: } dU = dQ - dW$$

dW and dQ are not exact differentials but dU is. The energy of the system depends on the state of the system, which is set by N , P and T for example, and U does not depend on the path leading to this particular N, P, T set.

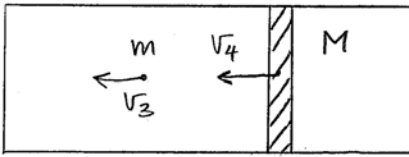
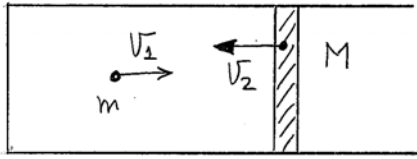
$$dU = -dW \quad (\text{if } dQ = 0 \text{ then } dW \text{ is full differential}).$$

$$dU = -dW = -PdV$$

If dV is negative (compression) U and T increase

If dV is positive (expansion) U and T decreases.

Microscopical (mechanical) interpretation



The piston is moving inward with velocity v_2 . We are going to find out that that velocity of a molecule after an elastic collision with a piston is $|v_3| = |v_1| + 2|v_2|$.

Collision is elastic \Rightarrow momentum and energy are conserved.

Momentum conservation $mv_1 - Mv_2 = -mv_3 - Mv_4$ (v_1, v_2, v_3, v_4 – positive numbers)

$$\text{Energy conservation} \quad \frac{1}{2}mv_1^2 + \frac{1}{2}Mv_2^2 = \frac{1}{2}mv_3^2 + \frac{1}{2}Mv_4^2$$

New parameter $\alpha = M/m$ – very large number.

$$v_1 - \alpha v_2 = -v_3 - \alpha v_4 \Rightarrow v_4 = \frac{1}{\alpha}(\alpha v_2 - v_3 - v_1) \Rightarrow v_4^2 = \frac{1}{\alpha^2}(\alpha v_2 - v_3 - v_1)^2$$

$$v_1^2 + \alpha v_2^2 = v_3^2 + \alpha v_4^2 \Rightarrow v_1^2 + \alpha v_2^2 = v_3^2 + \alpha v_2^2 + \frac{1}{\alpha} v_3^2 + \frac{1}{\alpha} v_1^2 + \frac{2}{\alpha} (v_3 v_1 - 2v_2 v_3 - 2v_2 v_1)$$

$$v_1^2 + \alpha v_2^2 = v_3^2 + \alpha v_2^2 + \frac{1}{\alpha} v_3^2 + \frac{1}{\alpha} v_1^2 + \frac{2}{\alpha} v_3 v_1 - 2v_2 v_3 - 2v_2 v_1$$

The terms $\frac{1}{\alpha} v_3^2$, $\frac{1}{\alpha} v_1^2$, $\frac{1}{\alpha} v_3 v_1$ are very small and can be neglected. Then we have

$$v_1^2 - v_3^2 = -2v_2 (v_3 + v_1)$$

$$(v_1 - v_3)(v_1 + v_3) = -2v_2 (v_3 + v_1)$$

And

$$v_3 = v_1 + 2v_2!!!$$

\rightarrow Elastic collisions with moving inward piston increase speed and therefore kinetic energy of molecules. Kinetic energy is measure of the temperature – Temperature of a gas increases upon compression.

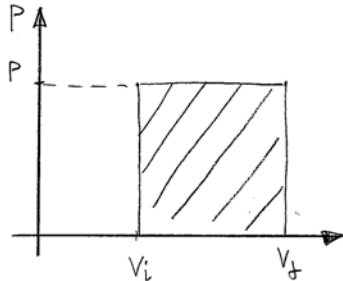
→ If gas expands same type of computation will give us $|v_3| = |v_1| - 2|v_2| \Rightarrow$ temperature decrease.

Compression in adiabatic ($dQ = 0$) process

$$dW = +PdV$$

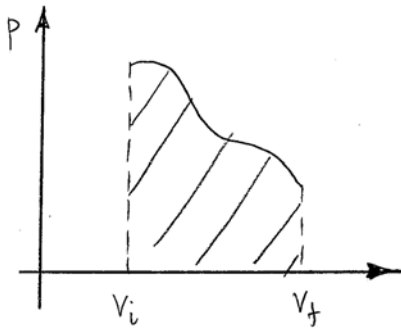
$$dU = -dW = -PdV$$

If P is constant: $W = P\Delta V$



$$W = P \cdot \Delta V = P \cdot (V_f - V_i)$$

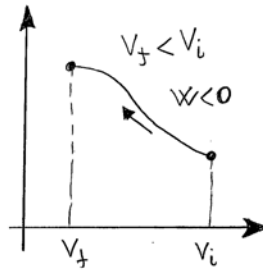
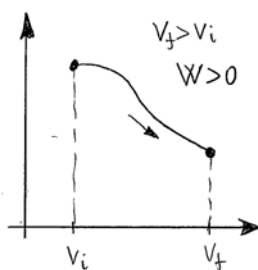
Arbitrary process



$$W = \int_{V_i}^{V_f} P(V) dV$$

$W = \int_{V_i}^{V_f} P(V) dV$. To use this equation pressure has to be same in all system in any moment of compression

(expansion). This process is called quasistatic process. It is relatively 'slow'. (Pressure in a cylinder equilibrates approximately with the speed of sound (300 m/s) so 'slow' process can be relatively fast). Please note that the sign of the integral depends on where you start.



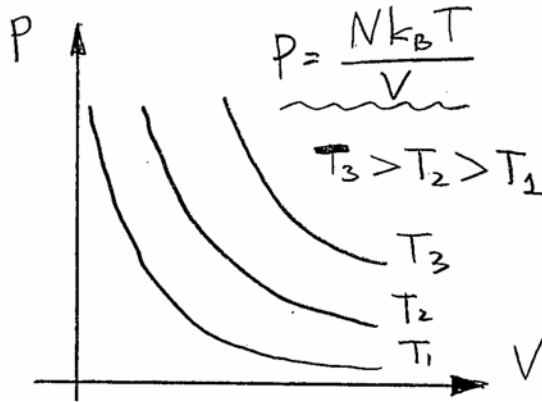
5) Compression of ideal gas

Real Process $\Delta T \neq 0$ $\Delta Q \neq 0$

5.1) Isothermal compression/expansion. $T = \text{Const}$, $\Delta T = 0$

The state of the system changes slowly. The system has time to exchange heat with surrounding and keep temperature uniform.

$$dW = PdV, \quad PV = nRT, \quad P = nRT/V$$



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

Comment: We have got $\ln V_f$ at the intermediate step. But it does not have physical meaning because of a problem with dimension. The $\ln \frac{V_f}{V_i}$ is OK, because the argument of the logarithm is now dimensionless.

Isothermal process $T = \text{const} \Rightarrow$ There is no change in the internal energy of a gas $\Delta U = 0$

From the 1st law $U = Q - W$

$$Q = W = nRT \ln \frac{V_f}{V_i}.$$

5.2) Adiabatic compression $\Delta Q = 0$

To compute the increase of the internal energy of a gas we have to know how its internal energy depends on temperature. Let us use Equipartition theorem.

$$U = \frac{1}{2} f N k_B T \quad u = \frac{1}{2} f N k T \quad N - \text{number of molecules.} \quad f = f_T + f_R + 2f_V.$$

$f_T = 3$ - Number of translational d. of. F.

f_R - Number of active rotation d. of. F.

f_V - Number of active vibrational d. o F.

$$dU = \frac{1}{2} f N k_B dT = -PdV \quad (dQ = 0)$$

From ideal gas law $P = \frac{1}{V} N k T$, after grouping the terms we have a differential equation $\frac{dV}{V} = -\frac{f}{2} \frac{dT}{T}$

and after integration we have

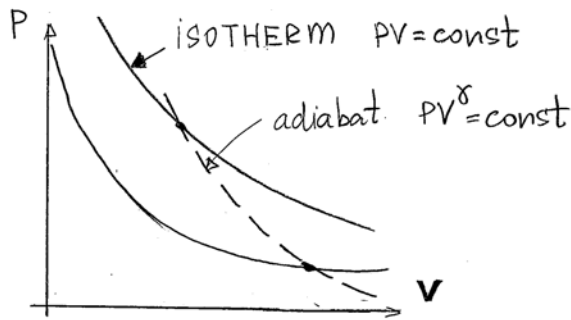
$$\ln \left(\frac{V_f}{V_i} \right) = -\frac{f}{2} \ln \left(\frac{T_f}{T_i} \right) = \frac{f}{2} \ln \left(\frac{T_i}{T_f} \right) = \ln \left(\left(\frac{T_i}{T_f} \right)^{\frac{f}{2}} \right)$$

From definition of the logarithm $e^{\ln x} = x$ we have

$\frac{V_f}{V_i} = \left(\frac{T_i}{T_f} \right)^{\frac{f}{2}}$ or $VT^{\frac{f}{2}} = \text{const}$ in adiabatic processes. Using ideal gas relations between P , V and T ,

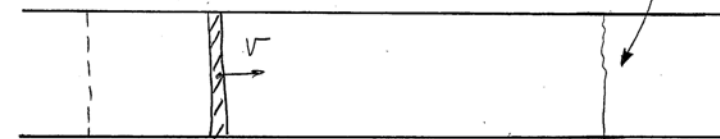
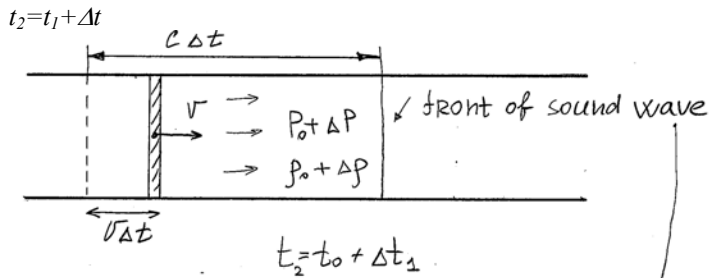
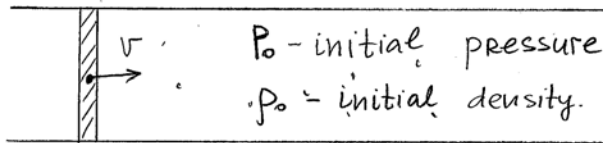
$\frac{PV}{T} = Nk = \text{const.}$, we may replace T in the $VT^{\frac{f}{2}} = \text{const}$ expression and obtain $V(PV)^{\frac{f}{2}} = \text{const}$. The standard way to write the relation between volume and pressure in adiabatic process is

$PV^\gamma = \text{const}$ where $\gamma = \frac{f+2}{f}$ is called adiabatic exponent.



6) Speed of Sound

$t_1=0$. At this moment we start moving a piston with constant velocity v



1) Mass conservation $m = \rho V$, ρ is the density of a gas, S cross sectional area of the cylinder.

$$\rho_0 S c \Delta t = (\rho_0 + \Delta \rho) (c - v) S \Delta t$$

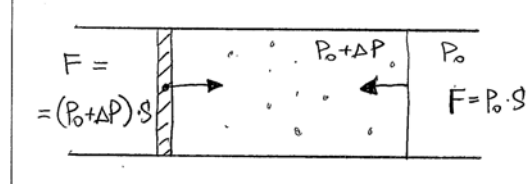
$$\rho_0 \cdot c = \rho_0 \cdot c - \rho_0 \cdot v + \Delta \rho c - \Delta \rho v$$

Because $v \ll c$ and $\Delta \rho \ll \rho$ $\Delta \rho v$ can be neglected.

$$\rho_0 v = \Delta \rho c$$

2) The second Newton's Law

$$F = ma = m \frac{dv}{dt}$$



Piston is moving with constant speed so the force acting on it from outside must be the same in magnitude as the force from inside that is $F = (P_0 + \Delta P)S$. The net force acting on the volume of the gas between piston and sound wave front is $F = \Delta PS$. This force acting on gas in the period of time Δt accelerated the gas up to velocity v so we have

$$F \Delta t = m \Delta v \Rightarrow \Delta PS \Delta t = mv \quad (\text{because initial velocity of the gas was } 0)$$

$$m = \rho V = \rho_0 S c \Delta t \quad (S c \Delta t - \text{initial volume of moving gas}). \text{ Combining the two equation above we have}$$

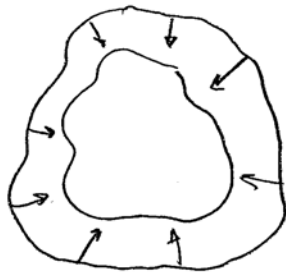
$$\Delta PS \Delta t = v \rho_0 S c \Delta t \Rightarrow \Delta P = v \rho_0 c. \quad \text{And using the relation we got from mass conservation } \rho_0 v = \Delta \rho c \text{ we have}$$

$$c = \sqrt{\frac{\Delta P}{\Delta \rho}} = \sqrt{\frac{dP}{d\rho}} \quad - \text{correct expression for gases, liquids and longitudinal sound waves in solids.}$$

Speed of sound in ideal gas

Important comment: Sound propagation is fast and therefore is an adiabatic process (no heat exchange with say walls of the tube). We need to find the ratio for $\frac{dP}{d\rho}$ in adiabatic process

$$1) \quad m = \rho V \Rightarrow dm = 0 = V d\rho + \rho dV \Rightarrow \frac{dV}{V} = -\frac{d\rho}{\rho}$$



compression.

$$2) \quad PV^\gamma = \text{const} \Rightarrow V^\gamma dP + P \gamma V^{\gamma-1} dV = 0 \Rightarrow \frac{dP}{P} = -\gamma \frac{dV}{V}$$

$$3) \quad \frac{dP}{P} = -\gamma \frac{dV}{V} = \gamma \frac{d\rho}{\rho} \Rightarrow \frac{dP}{d\rho} = \gamma \frac{P}{\rho}$$

$$c = \sqrt{\frac{dP}{d\rho}} = \sqrt{\gamma \frac{P}{\rho}}$$

Air is mainly composed of N_2 . So let's make an estimate for the speed of sound in N_2 at ambient pressures. For N_2 at room temperature vibrational degree of freedom are 'frozen out' but rotational are active.

$$f = 3 + 2 = 5 \quad (3 - \text{Translational}, 2 - \text{rotational}). \quad \text{Then } \gamma = \frac{f+2}{f}$$

At ambient condition 1 mole of ideal gas takes volume 25 liters = $25 \cdot 10^{-3} \text{ m}^3$

Density of the nitrogen $\rho = \frac{28 \cdot 10^{-3} \text{ kg}}{25 \cdot 10^{-3} \text{ m}^3} = 1.12 \frac{\text{kg}}{\text{m}^3}$

Pressure $P = 10^5 \text{ Pa}$

$$c = \sqrt{\gamma \frac{P}{\rho}} = \sqrt{\frac{7}{5}} \sqrt{\frac{10^5}{1.12}} = 353 \text{ m/s}$$

Experimental value is 344 m/s.