PHYS-2010: General Physics I Course Lecture Notes Section XIII

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Abstract

These class notes are designed for use of the instructor and students of the course PHYS-2010: General Physics I taught by Dr. Donald Luttermoser at East Tennessee State University. These notes make reference to the *College Physics*, 11th Edition (2018) textbook by Serway and Vuille.

XIII. Gas Laws and the Kinetic Theory of Gases

- A. State Variables: Quantities that describe the condition or state of a system.
 - 1. Pressure: P = F/A [SI units: Pa = N m⁻²] or [cgs units: dyne cm⁻²].
 - 2. Temperature: A measure of the amount of heat in a system [K] or [°C]. More precisely, it is a measure of the average velocity of the particles in matter (see §XIII.G).
 - 3. Volume (or Density):
 - a) Mass Density: ρ ('rho') \equiv amount of mass per unit volume [SI units: kg m⁻³] or [cgs units: g cm⁻³].
 - b) Number Density: N ('capital N') \equiv number of particles per unit volume [SI units: m⁻³] or [cgs units: cm⁻³]. Note that one could include 'atoms,' 'molecules,' or 'particles' in the numerator of the units for this parameter, but these terms are not really *units* (like 'radian' and angular 'degree'), and as such, I have not included any of these labels in the 'units' for number density, though their inclusion are implied. (Note that your textbook uses capital-N as the <u>total</u> number of particles present and not the way I define it here.)
 - c) The total number of particles and volume can be expressed separately as well:
 - i) Volume: $V \equiv$ Total 'space' that the gas fills [SI units: m³] or [cgs units: cm³]

ii) Particle Number: n ('small n') ≡ number of particles present ⇒ typically measured in moles → the amount of material whose mass in grams is numerically equal to the molecular mass of the substance (*i.e.*, the atomic mass of nitrogen N is 14 since its nucleus is composed of 7 protons and 7 neutrons, the molecular mass of nitrogen N₂ is (14+14=) 28 → a mole of atomic nitrogen is 14 grams and a mole of molecular nitrogen is 28 grams) [mol].

Example XIII-1. Estimate the "total weight" of the atmosphere, using your knowledge of barometers and the given radius of the Earth.

Solution:

We just need to use the pressure equation given by Eq. (XI-7). The weight w is the force F_g of the atmosphere pressing down on us. The area in this equation is the total surface area of the Earth $A_{\oplus} = 4\pi R_{\oplus}^2$:

$$w = F_g = PA = P_{\circ} \cdot 4\pi R_{\oplus}^2 = (1.01 \times 10^5 \text{ N/m}^2)(4\pi)(6.4 \times 10^6 \text{ m})^2$$
$$= 5.2 \times 10^{19} \text{ N}.$$

B. Physical Constants Used in Gas Laws.

1. Avogadro's Number: A mole of gas contains the same number of molecules: $N_{\rm A}$.

 $N_{\rm A} = 6.02252 \times 10^{23} \mbox{ molecules/mole}$.

2. Universal Gas Constant:

$$R = 8.3143 \text{ J/(mol \cdot K)}$$
 (SI system)

or

$$R = 8314.3 \text{ J/(kmol \cdot K)}$$

= 8.2056 × 10⁻² m³ · atm/(kmol · K)
= 8.2056 × 10⁻² li · atm/(mol · K)
= 8.3143 × 10⁷ erg/(mol · K) (cgs system).

3. Boltzmann's Constant:

$$k_{\rm B} = \frac{R}{N_{\rm A}} = 1.3807 \times 10^{-23} \text{ J/K}$$
 (SI system)
= $1.3807 \times 10^{-16} \text{ erg/K}$ (cgs system).

C. The Various Forms of Density.

1. The density-volume state variable mentioned above can all be interrelated to one another

$$\rho = \mu m_{\rm H} N = \overline{m} N = \frac{\mu m_{\rm H} n N_{\rm A}}{V} . \qquad (\text{XIII-1})$$

a) $m_{\rm H} \equiv \text{mass of the hydrogen atom (the most common atom in the Universe):}$

$$m_{\rm H} = 1.6726 \times 10^{-27} \text{ kg}$$

= 1.6726 × 10⁻²⁴ g
= 1.008 amu ,

where amu \equiv **atomic mass unit** is another way to describe the mass of a particle.

i) The *size* of the amu in terms of kilograms is defined in two different ways. Whenever you use the amu unit, make sure you notice which definition is being used (the data table or periodic table you are using will typically mention this in a footnote).

- ::) The first met
 - ii) The first method is scaled with respect to ${}^{12}C$ (*i.e.*, the 6-proton, 6-neutron isotope of carbon) where ${}^{12}C$ is exactly 12.0000 amu.
 - iii) The second method is scaled with respect to ${}^{16}O$ (*i.e.*, the 8-proton, 8-neutron isotope of oxygen) where ${}^{16}O$ is exactly 16.0000 amu.
 - iv) In both cases, the hydrogen atom (¹H) is slightly greater than 1 amu since the mass of the neutron (which C & N have) is slightly greater than the mass of the proton (see §XI.A.3 on page XI-1 of these notes).
 - b) μ ('mu') \equiv mean molecular weight (unitless number) \implies takes account of systems composed of different types of particles.
 - c) $\overline{m} \equiv \text{mean (average) mass of gas particles:}$

$$\overline{m} = \frac{\sum_{i} m_{i} N_{i}}{\sum_{i} N_{i}} .$$
 (XIII-2)

- i) \sum_i is the summation symbol \rightarrow it means to add together each term in the series of terms.
- ii) $m_i \equiv \text{mass of a specific type of gas particle } (e.g., He, N_2, O_2, H_2O, \text{etc.}).$
- iii) $N_i \equiv$ number density of each specific particle.

iv) Note that
$$N = \sum_{i} N_{i}$$
 and

$$\mu = \frac{\overline{m}}{m_{\rm H}}.$$
(XIII-3)

2. The form of density (and/or volume) you use depends upon the specific problem being solved.

D. Boyle's (Constant Temperature) Law.

- 1. In words: The pressure exerted by a gas at 'constant temperature' is inversely proportional to the volume in which it is enclosed.
- **2.** Mathematically:

$$PV = \text{constant}$$

or

$$P_1 V_1 = P_2 V_2 , \qquad (XIII-4)$$

where '1' and '2' refer to two different states of the same sample of gas at constant temperature.

3. This is the *constant temperature* gas law.

Example XIII–2. An air bubble has a volume of 1.50 cm³ when it is released by a submarine 100 m below the surface of a lake. What is the volume of the bubble when it reaches the surface? Assume that the temperature and the number of air molecules in the bubble remain constant during the ascent.

Solution:

We just need to apply Boyle's law (see Eq. XIII-4),

$$P_1V_1 = P_2V_2 ,$$

where '1' refers to the condition at the location of the submarine and '2' refers to the surface of the lake. At the surface, $P_2 = P_{\circ} = 1$ atm = 1.01×10^5 N/m². We are told that $V_1 = 1.50$ cm³ and we are to calculate

 V_2 . As such, we need to determine P_1 . Using Pascal's Principle (Eq. XI-10), we can determine this pressure of the lake at the submarine's location:

$$P_1 = P_\circ + \rho g h$$

where $\rho = 1000 \text{ kg/m}^3$ is the density of water, h = 100 m is the depth of the submarine, and $g = 9.80 \text{ m/s}^2$. Solving Boyle's law for the air bubble volume at the surface in conjunction with Pascal's Principle gives

$$V_{2} = \frac{P_{1}}{P_{2}}V_{1} = \frac{P_{1}}{P_{\circ}}V_{1}$$

= $\frac{P_{\circ} + \rho gh}{P_{\circ}}V_{1} = \left(1 + \frac{\rho gh}{P_{\circ}}\right)V_{1}$
= $\left(1 + \frac{(1000 \text{ kg/m}^{3})(9.80 \text{ m/s}^{2})(100 \text{ m})}{1.01 \times 10^{5} \text{ N/m}^{2}}\right)$ (1.50 cm³)
= $(1 + 9.70)(1.50 \text{ cm}^{3})$
= 16.1 cm^{3} .

E. Charles' (Constant Pressure) Law.

- **1.** In words: At **constant pressure**, a volume of gas per unit temperature (in K) remains constant.
- **2.** Mathematically:

$$\frac{V}{T} = \text{ constant}, \quad \frac{V_1}{V_2} = \frac{T_1}{T_2}$$
(XIII-5)

 $\implies T$ must be measures in Kelvin here.

3. This is the *constant pressure* gas law.

F. Gay-Lussac's (Constant Volume) Law.

- 1. In words: At constant volume, the pressure of the gas per unit temperature (in K) remains constant.
- **2.** Mathematically:

$$\frac{P}{T} = \text{ constant}, \quad \frac{P_1}{P_2} = \frac{T_1}{T_2}$$
 (XIII-6)

 $\implies T$ must be measures in Kelvin here.

3. This is the *constant volume* gas law.

G. Equation of State.

- 1. Gas pressure typically depends upon the temperature of the material and the volume of the container that holds the material.
 - a) P as a function of T and V (or ρ or N) is called the equation of state of the material.
 - **b)** In general, the equation of state for a material is very complicated.
 - c) For low pressures (or low densities), the equation of state becomes very simple \implies the ideal gas law.
- 2. An ideal gas has the following characteristics:
 - a) The number of molecules (*i.e.*, particles) in the gas is large and the average separation between them is large compared to their dimension \implies particles are very far apart compared to their size.
 - **b)** The particles move randomly following Newton's laws of motion.

- c) The molecules interact only by short-range forces during elastic collisions \implies forces between the particles are negligible except during a collision.
- d) Particle-wall collisions are elastic as well.
- e) The composition of the gas is homogeneous (*i.e.*, smooth and the same everywhere).
- **3.** The equation of state of an ideal gas is (Form 1):

$$PV = nRT$$
 . (XIII-7)

a)
$$P \equiv \text{pressure } [\text{Pa} = \text{N/m}^2 = \text{J/m}].$$

- **b)** $V \equiv \text{volume } [\text{m}^3].$
- c) $n \equiv$ number of 'moles' in the gas as explained in §XIII.A.3.c.ii [mol]. Once again:
 - i) Equal volume of gas at the same temperature and pressure contain the same number of molecules.
 - ii) One mole quantity of all gases at standard temperature (0°C = 273.15 K) and pressure (1 atm = 101.3 kPa) [≡ STP] contain the same number of molecules.
- d) $R \equiv \text{universal gas constant} = 8.314 \text{ J/mol} \cdot \text{K}.$
- e) $T \equiv \text{temperature [K]}.$

Example XIII–3. A popular brand of cola contains 6.50 g of carbon dioxide dissolved in 1.00 L of soft drink. If the evaporating carbon dioxide is trapped in a cylinder at 1.00 atm and 20° C, what

volume does the gas occupy?

Solution:

Carbon, C, has 12 nucleons in it and oxygen, O, has 16. Since there are 2 oxygen atoms and 1 carbon atom in carbon dioxide (CO₂), its molecular mass is $12 + 2 \cdot 16 = 44$ gm/mol. As such, the number of moles of CO₂ present is

$$n = \frac{6.50 \text{ gm}}{44.0 \text{ gm/mol}} = 0.148 \text{ mol.}$$

Thus, at the given temperature $(T = T_{\rm C} + 273.15 = 20 + 273.15 = 293 \text{ K})$ and pressure $(P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ Pa})$, the volume can be determined from Form 1 of the ideal gas law (Eq. XIII-7):

$$PV = nRT$$
, $V = \frac{nRT}{P}$,

or

$$V = \frac{(0.148 \text{ mol})(8.314 \text{ J/(mol K)})(293 \text{ K})}{1.013 \times 10^5 \text{ N/m}^2} = 3.55 \times 10^{-3} \text{ m}^3$$
$$= 3.55 \text{ L}.$$

4. The equation of state of an ideal gas can also be expressed as (Form 2):

$$P = Nk_{\rm B}T . \tag{XIII-8}$$

- a) $N \equiv$ particle density as described in §XIII.A.3.b $[m^{-3}]$.
- **b)** $k_{\rm B} \equiv \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J/K}.$

5. Finally, the equation of state of an ideal gas is given by (Form 3):

$$P = \frac{\rho k_{\rm B} T}{\mu m_{\rm H}} . \tag{XIII-9}$$

- a) $\rho \equiv \text{mass density as described in §XIII.A.3.a } [m^{-3}].$
- b) $\mu m_{\rm H}$ measures the average mass of the particles in the sample.

H. Kinetic Theory of Gases.

- 1. This theory describes the microscopic motion of gas particles. It assumes that the gas behaves *ideally*.
- 2. At the heart of this theory: The temperature of the gas is related to the average velocity of a gas particle.
 - a) Thermal energy = average kinetic energy of particles in the gas:

$$TE = \overline{KE}$$

or

$$\frac{3}{2}k_{\rm B}T = \frac{1}{2}m\overline{v^2} , \qquad (\text{XIII-10})$$

where the 'overline' indicates *average*.

b) The average velocity of a gas particle is

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} . \qquad (\text{XIII-11})$$

i) The <u>average</u> component velocities are equal to each other for random motion:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \ .$$

ii) So, Eq. (XIII-10) can be rewritten as

$$\overline{v^2} = 3\overline{v_x^2} . \qquad (XIII-12)$$

- c) A degree of freedom in a gas refers to the number of independent means by which a gas particle can possess energy.
 - i) If it moves in the x, y, and z directions, it has 3 degrees of freedom.
 - ii) So, we can write three separate energy equations:

$$E_x = \frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_{\rm B}T$$

$$E_y = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}k_{\rm B}T$$

$$E_z = \frac{1}{2}m\overline{v_z^2} = \frac{1}{2}k_{\rm B}T$$

and the average kinetic energy is then the sum of the energies in these three different directions:

$$E = E_x + E_y + E_z = \frac{1}{2}m\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) = \frac{1}{2}m\left(\overline{v^2}\right) = \frac{1}{2}k_{\rm B}T + \frac{1}{2}k_{\rm B}T + \frac{1}{2}k_{\rm B}T = \frac{3}{2}k_{\rm B}T ,$$

or

$$\overline{v^2} = \frac{3k_{\rm B}T}{m} . \qquad (\text{XIII-13})$$

d) The square root of $\overline{v^2}$ is called the **root-mean-square** (rms) velocity:

$$v_{\rm rms} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\rm B}T}{m}}$$
 (XIII-14)

 \implies when we talk about velocity of gas particles, we will always mean $v_{\rm rms}$. **Example XIII–4.** Starting with $v_{\rm rms} = \sqrt{3k_{\rm B}T/m}$, where $k_{\rm B}$ is Boltzmann's constant, T the temperature, and m the molecular mass, show that the rms speed can be put in the form $v_{\rm rms} = \sqrt{3P/\rho}$, where P is the pressure and ρ is the density of an ideal gas.

Solution:

In these equations, $m = \overline{m} = \mu m_{\rm H}$, the mean molecular mass as defined in Eqs. (XIII-1,2). With this realization, we can use Form 3 of the ideal gas law as shown by Eq. (XIII-9), then

$$v_{\rm rms} = \sqrt{\frac{3k_{\rm B}T}{m}} = \sqrt{\frac{3k_{\rm B}T}{\overline{m}}} = \sqrt{\frac{3k_{\rm B}T}{\mu m_{\rm H}}}$$
$$= \sqrt{\frac{\rho}{\rho} \frac{3k_{\rm B}T}{\mu m_{\rm H}}} = \boxed{\sqrt{\frac{3P}{\rho}}}.$$

3. We have seen that **thermal energy** is identical the **average kinetic energy** of the gas:

TE =
$$\overline{\text{KE}} = \frac{3}{2}k_{\text{B}}T$$
 [per particle] = $\frac{3}{2}RT$ [per mole]. (XIII-15)

from this the ideal gas law can be written as

$$P = \frac{2}{3}N\,\overline{\text{KE}} \,. \tag{XIII-16}$$

(Once again note that my capital N and the textbook's capital N do not mean the same thing: $N_{\text{notes}} = N_{\text{book}}/V$, where N_{book} is the total number of particles in the sample [not particle density as used in the notes].)

a) The product $N \overline{\text{KE}}$ is the *total translational kinetic energy* per <u>unit volume</u> of the gas due to the random thermal motion of the molecules. b) If we ignore the intermolecular bonds in molecules, Eq. (XII-6) shows that this kinetic energy represents one of the <u>three</u> components of the total **internal energy** U of a gas:

$$U = \overline{\mathrm{KE}}_{\mathrm{trans}} + \overline{\mathrm{KE}}_{\mathrm{rot}} + \overline{\mathrm{KE}}_{\mathrm{vib}} \ .$$

 c) If there are no rotational nor internal vibrational motion of the particles in the gas (a so-called monatomic gas), then we can write the ideal gas law as

$$PV = nRT = \frac{2}{3}\overline{\mathrm{KE}} = \frac{2}{3}U \ ,$$

or

$$U = \frac{3}{2}nRT . \qquad (XIII-17)$$

I. Hydrostatic Equilibrium.

- 1. Whenever you have a volume of gas, there are two competing forces:
 - a) The force per unit volume from the internal pressure: $F/V = \Delta P \cdot A/V.$
 - b) The weight per unit volume of the gas trying to pull the gas to the lowest potential: $F_g/V = -mg/V = -\rho g$.
- 2. Assume we have a column of gas, then $A = \pi r^2$ and $V = \pi r^2 \Delta z$, where r is the radius of the column cylinder and Δz is the length of the column. Then equating the two forces above, we get

$$\frac{\Delta P}{\Delta z} = -\rho g \ . \tag{XIII-18}$$

a) This is the equation of hydrostatic equilibrium \implies internal pressure is balanced by the weight of the gas.

 b) We can use a modified version of Form 3 of the ideal gas law to rewrite Eq. (XIII-17) as

$$\frac{\Delta P}{\Delta z} = -\frac{\overline{m}g}{k_{\rm B}T}P \ . \tag{XIII-19}$$

c) This equation can be solved with integral calculus by letting $\Delta z \rightarrow 0$. Since this is beyond the scope of this class, we will just write the solution to this equation:

$$P(z) = P_{\circ} e^{-\overline{m}gz/k_{\rm B}T} , \qquad (\text{XIII-20})$$

where P_{\circ} is the pressure at z = 0 and e is the base of the natural logarithm system (see Page II-3 of these notes).

d) We could also carried out the integration for number density which results as

$$N = N_{\circ} e^{-\overline{m}gz/k_{\rm B}T} , \qquad (\text{XIII-21})$$

this equation is called the **barometric formula** \implies it gives the number of molecules per unit volume as a function of height z.

Example XIII–5. (a) At what height above sea level is the atmospheric pressure half the pressure at sea level? Assume the temperature is a constant 0° C. (b) How high must you go for the pressure to drop to one-fourth the pressure at sea level? (Use $m = \overline{m} = 4.80 \times 10^{-26}$ kg for the mean molecular mass of air.)

Solution (a):

We start by converting our temperature to the absolute scale, $T = 0^{\circ}$ C = 273 K. Using the solution to the hydrostatic equilibrium equation (Eq. XIII-20), we want $P = 0.5P_{\circ}$, so

$$e^{-\overline{m}gz/k_{\rm B}T} = \frac{P}{P_{\circ}} = \frac{0.5P_{\circ}}{P_{\circ}} = 0.5$$

$$-\frac{\overline{m}gz}{k_{\rm B}T} = \ln(0.5) = -0.693$$

$$z = 0.693 \frac{k_{\rm B}T}{\overline{m}g} = 0.693 \frac{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{(4.80 \times 10^{-26} \text{ kg})(9.80 \text{ m/s}^2)}$$

$$= 5.55 \times 10^3 \text{ m} = 5.55 \text{ km}.$$

Solution (b):

Now we want $P = 0.25 P_{\circ}$, so

$$e^{-\overline{m}gz/k_{\rm B}T} = \frac{P}{P_{\rm o}} = \frac{0.25P_{\rm o}}{P_{\rm o}} = 0.25$$

$$-\frac{\overline{m}gz}{k_{\rm B}T} = \ln(0.25) = -1.386$$

$$z = 1.386 \frac{k_{\rm B}T}{\overline{m}g} = 1.386 \frac{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{(4.80 \times 10^{-26} \text{ kg})(9.80 \text{ m/s}^2)}$$

$$= 1.11 \times 10^4 \text{ m} = \boxed{11.1 \text{ km}}.$$