THERMAL PROPERTIES OF MATTER I

Intended Learning Outcomes – after this lecture you will learn:
1. equation of state
2. ideal gas temperature and ideal gas equation
3. *p*-*V* diagram
4. kinetic theory and the relation of ideal gas temperature and kinetic energy

Textbook Reference: 18.1 – 18.3 (Excluding: **Van der Waals Equation** on P. 612, **Molecules and Intermolecular Force** on P. 613, and **Collisions Between Molecules** on P. 620)

One **mole** is the amount of substance that contains as many elementary entities as there are atoms in 0.012 kg of carbon-12.
The **Avogadro number** $N_A = 6.022 \times 10^{23}$ is the number of molecules in one mole of the substance
The **molar mass** M of a substance is the mass of 1 mole, i.e., mass number of the substance

Equation of state

How to specify the state of a substance? – in terms of <u>macroscopic</u> (measurable) quantities p, V, T
An equation relating p, V, T, $f(p,V,T) = 0$ is called an **equation of state**, i.e., only two among p, V, T are independent.

A simple starting point – an ***ideal* gas**

"ideal" means never exist, can only be approximated

Experimental condition: inert gas at low density (or low pressure)

Consider different ideal gases with number of moles n, pressure p and volume V. Experiments show that ideal gases with the same pV/n are in thermal equilibrium (empirical in thermodynamics, without knowing why, microscopic theory provides the explanation)

By zeroth law, can define a temperature so that $T = g(pV/n)$ where g is a one-to-one function.
Simplest choice: define $T \propto pV/n$, called **ideal gas temperature**
Will be shown later that it is the same as the absolute temperature defined more fundamentally by the second law of thermodynamics. Hence the same unit **kelvin** (K)

Ideal gas law: $\boxed{pV = nRT}$ (Recall: why we can measure T by p and keeping V constant)

Proportional constant, called **universal gas constant**, R, defined in a way so that T of triple point of water is exactly 273.16 K, which fixes the temperature scale (⚠ this is the temperature measured by a constant volume thermometer, since when V and n are fixed, $T \propto p$)
Measured value: $R \cong 8.314\ \mathrm{J/mol \cdot K}$

Equivalently

total mass of gas

$$pV = \frac{m}{M}RT \quad \Rightarrow \quad \rho = \frac{m}{V} = \frac{pM}{RT}$$

molar mass of gas

For a *fixed amount* of gas

$$\boxed{\frac{pV}{T} = \text{constant}} \qquad \text{i.e.,} \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

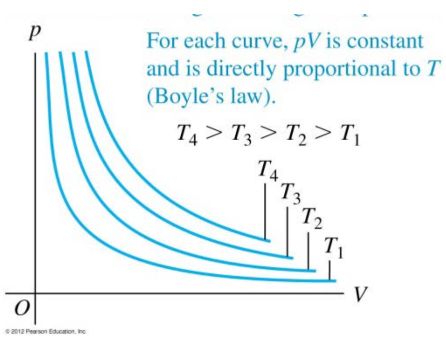
Standard temperature and pressure (STP) is defined as $T = 0\ ℃ = 273.15\ \mathrm{K}$ and $p = 1\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{Pa}$. One mole of ideal gas under STP has a volume (**molar volume**)

$$V = RT/p = (8.314\ \mathrm{J/mol})(273.15\ \mathrm{K})/(1.013 \times 10^5\ \mathrm{Pa}) = 0.0224\ \mathrm{m^3} = 22.4\ \mathrm{L}$$

⚠ irrespective of other details of the gas, as long as it is an ideal gas.

Equation of state has three variables *p*, *V*, and *T*, difficult to plot. If plot as *p* vs *V* at constant *T*, called a ***p-V* diagram**, each curve at a particular *T* is called an **isotherm**.

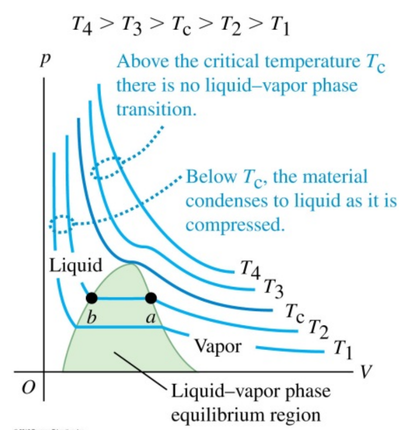
ideal gas

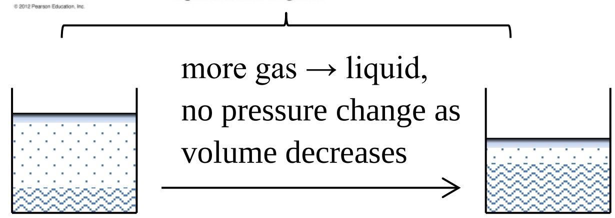


$$p = \frac{nRT}{V} \propto \frac{1}{V}$$

called **Boyle's law**
⚠ always be a gas, will not liquefy

real gas





Example 18.3 P. 611

A tank has volume 11.0 L initially contains air at 21 °C and 1 atm. The initial number of moles of air in the tank is

$$n_1 = \frac{p_1 V_1}{RT_1} = \frac{(1.013 \times 10^5 \text{ Pa})(11.0 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol·K})(294 \text{ K})} = 0.46 \text{ mol}$$

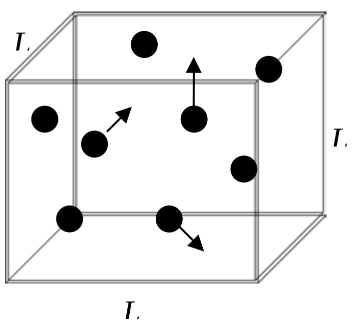
It is then filled with air from a compressor to a final temperature 42 °C and pressure 2.10×10^7 Pa. The final number of moles of air is

$$n_2 = \frac{p_2 V_2}{RT_2} = \frac{(2.11 \times 10^7 \text{ Pa})(11.0 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol·K})(315 \text{ K})} = 88.6 \text{ mol}$$

Given air has average molar mass 28.8 g/mol, the amount of air pumped in is $M(n_2 - n_1) = (0.0288 \text{ kg/mol})(88.6 - 0.46 \text{ mol}) = 2.54 \text{ kg}$

Kinetic Theory of Ideal Gas

Demonstration: [kinetic theory model]

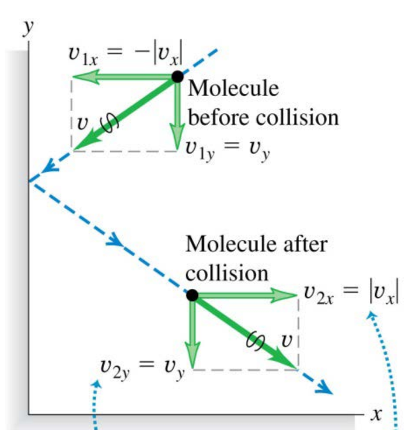


Model a gas as N *identical* particles, each of mass m, obeying Newtonian (classical) mechanics

Particles hitting the wall → pressure

What is so "ideal" about an ideal gas? Assume no interaction among particles except when they collide, and all collisions are perfectly elastic, i.e., kinetic energy is conserved.

⚠ An ideal gas has no solid or liquid phases because _____________



One particle collide with a wall, change in momentum

$$\Delta P_x = (mv_x) - (-mv_x) = 2mv_x$$

Time between consecutive collisions

$$\Delta t = 2L/v_x$$

$$\Rightarrow \quad F = \frac{\Delta P_x}{\Delta t} = \frac{mv_x^2}{L}$$

With N particles, each with v_{xi}, pressure on wall is

$$p = \frac{F}{A} = \frac{1}{L^2}\sum_{i=1}^{N}\frac{mv_{xi}^2}{L} = \frac{Nm}{V}\left[\frac{1}{N}\sum_{i=1}^{N} v_{xi}^2\right]$$

Since x, y, z directions are equivalent (ignoring gravity)

$$\frac{1}{N}\sum_{i=1}^{N} v_{xi}^2 = \frac{1}{N}\sum_{i=1}^{N} v_{yi}^2 = \frac{1}{N}\sum_{i=1}^{N} v_{zi}^2 = \frac{1}{3}\underbrace{\left[\frac{1}{N}\sum_{i=1}^{N}\left(v_{xi}^2 + v_{yi}^2 + v_{zi}^2\right)\right]}_{(v^2)_{\text{av}}}$$

We get $pV = \frac{1}{3}Nm(v^2)_{\text{av}} = \frac{2}{3}N\underbrace{\left[\frac{1}{2}m(v^2)_{\text{av}}\right]}_{\text{total translational KE } K_{\text{tr}}} = \frac{2}{3}K_{\text{tr}}$ $\quad pV = nRT$

$\boxed{K_{\text{tr}} = \frac{3}{2}nRT}$ translational KE of n moles of ideal gas

KE per particle $\quad \frac{K_{\text{tr}}}{N} = \frac{1}{2}m(v^2)_{\text{av}} = \frac{3nRT}{2N} = \frac{3}{2}\left(\frac{R}{N_A}\right)T = \frac{3}{2}kT$

Avogadro number

$$N_A \equiv \frac{N}{n} = 6.022 \times 10^{23}$$

Boltzmann constant

$$k \equiv \frac{R}{N_A} = 1.381 \times 10^{-23}\ \text{J/K}$$

To summarize the corresponding equations in terms of R and k

ideal gas law: $\boxed{pV = nRT = NkT}$

total translational KE of ideal gas: $\boxed{K_{\text{tr}} = \frac{3}{2}nRT = \frac{3}{2}NkT}$

⚠ Confusion: when to use R and when to use k?

- if the amount of gas is expressed in terms of number of particles N, then use the Boltzmann constant k
- if in terms of number of moles n, then use the universal gas constant R

Define the **root-mean-square** (rms) speed as $v_{\text{rms}} \equiv \sqrt{(v^2)_{\text{av}}}$, i.e.,

$$v_{\text{rms}} = \sqrt{\underbrace{\frac{1}{N}\sum_{i=1}^{N}}_{\text{mean}}\left(v_i^2\right)} \neq \frac{1}{N}\sum_{i=1}^{N} v_i \qquad \boxed{v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}}$$

note the order: root mean square

mass per particle

molar mass

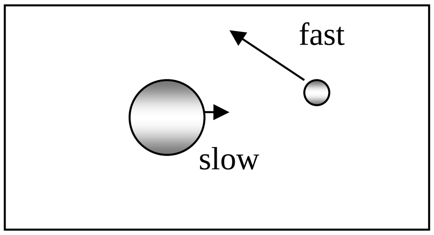
E.g. N_2, molar mass 28×10^{-3} kg/mol, at room temperature (________ K)

$$v_{\text{rms}} = \sqrt{\frac{3(8.314\ \text{J/mol}\cdot\text{K})(300\ \text{K})}{28.0\times10^{-3}\ \text{kg/mol}}} = 516\ \text{m/s}$$

⚠ very fast, but diffusion of a gas in room temperature is much slower

⚠ slower than escape speed of earth (1.12×10^{4} m/s), atmosphere exists

Average KE of particle ($\frac{3}{2}kT$) independent of mass!! Depends on T only.



same T , i.e., in thermal equilibrium -- average energy content of particles do not change on collision

<u>Question</u>

A gas mixture consists of molecules of types 1, 2, and 3, with molecular masses $m_1 > m_2 > m_3$.

Then for average KE, ___<____<____, and for v_{rms}, ___<___<___

Clicker Questions:

Q18.1

A quantity of an ideal gas is contained in a balloon. Initially the gas temperature is 27°C. You double the pressure on the balloon and change the temperature so that the balloon shrinks to one-quarter of its original volume. What is the new temperature of the gas?

A. 54°C

B. 27°C

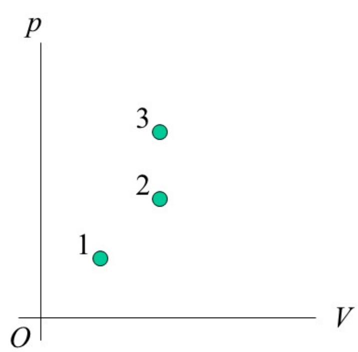
C. 13.5°C

D. –123°C

E. –198°C

Q18.2

This *p-V* diagram shows three possible states of a certain amount of an ideal gas. Which state is at the *highest* temperature?



A. state #1

B. state #2

C. state #3

D. Two of these are tied for highest temperature.

E. All three of these are at the same temperature.

Q18.5

Consider two specimens of ideal gas at the same temperature. Specimen #1 has the same total mass as specimen #2, but the molecules in specimen #1 have greater molar mass than the molecules in specimen #2. In which specimen is the *total translational kinetic energy of the entire gas* greater?

A. specimen #1

B. specimen #2

C. The answer depends on the particular mass of gas.

D. The answer depends on the particular molar masses.

E. Both C and D are correct.

Q18.6

You have a quantity of ideal gas in a cylinder with rigid walls that prevent the gas from expanding or contracting. If you double the rms speed of molecules in the gas, the gas pressure

A. increases by a factor of 16.

B. increases by a factor of 8.

C. increases by a factor of 4.

D. increases by a factor of 2.

E. increases by a factor of $2^{1/2}$.

Ans: Q18.1) D, Q18.2) C, Q18.5) B, Q18.6) C