

AE1241 Physics

Chapter 18 Kinetics Theory of Gases

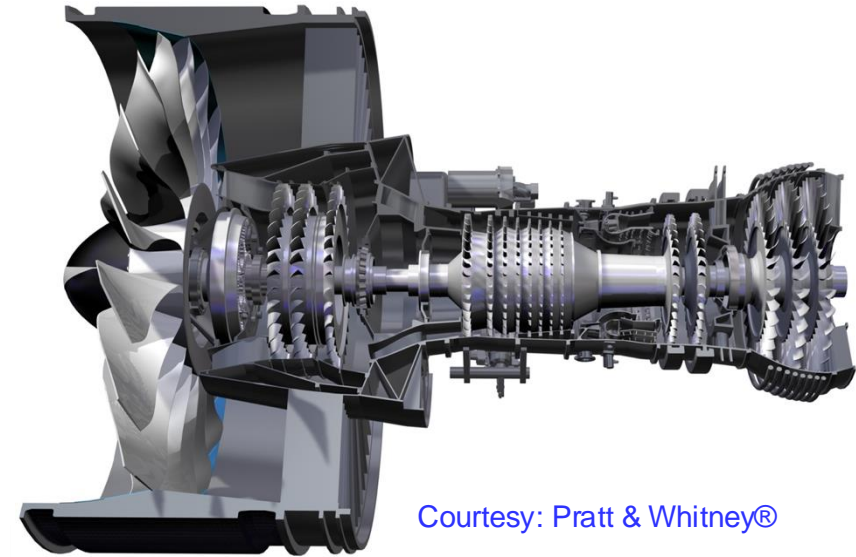
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27th February, 2025

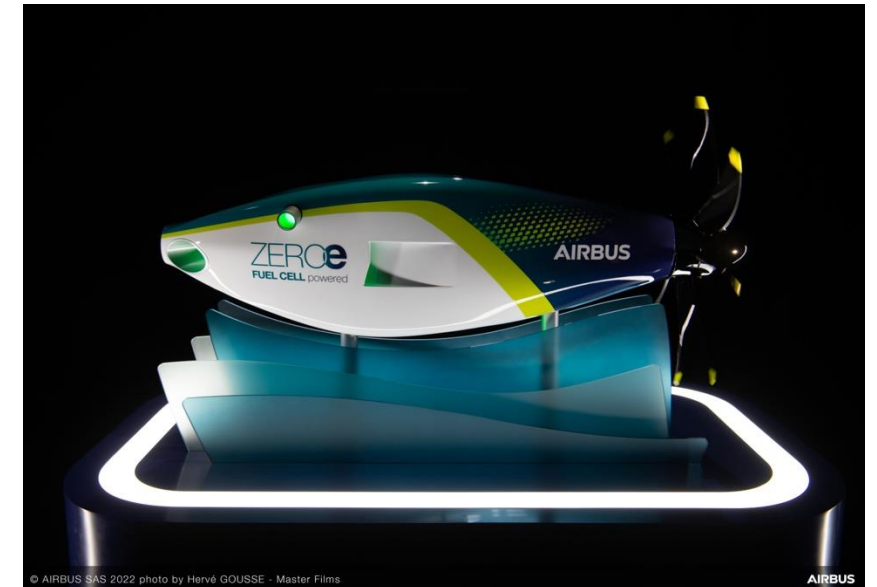
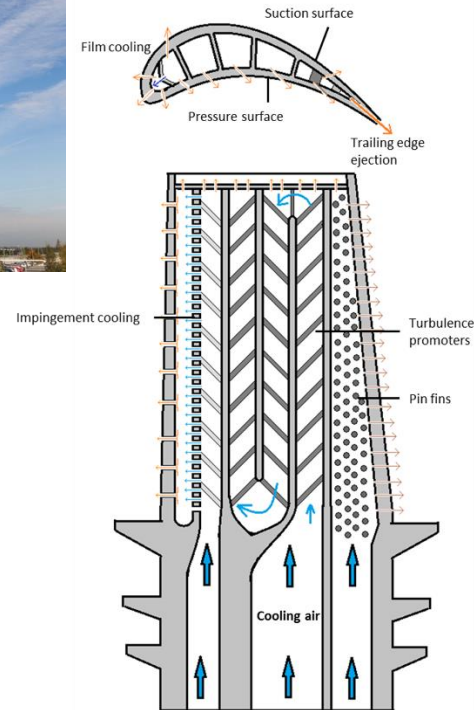
Relevance of thermodynamics to aerospace



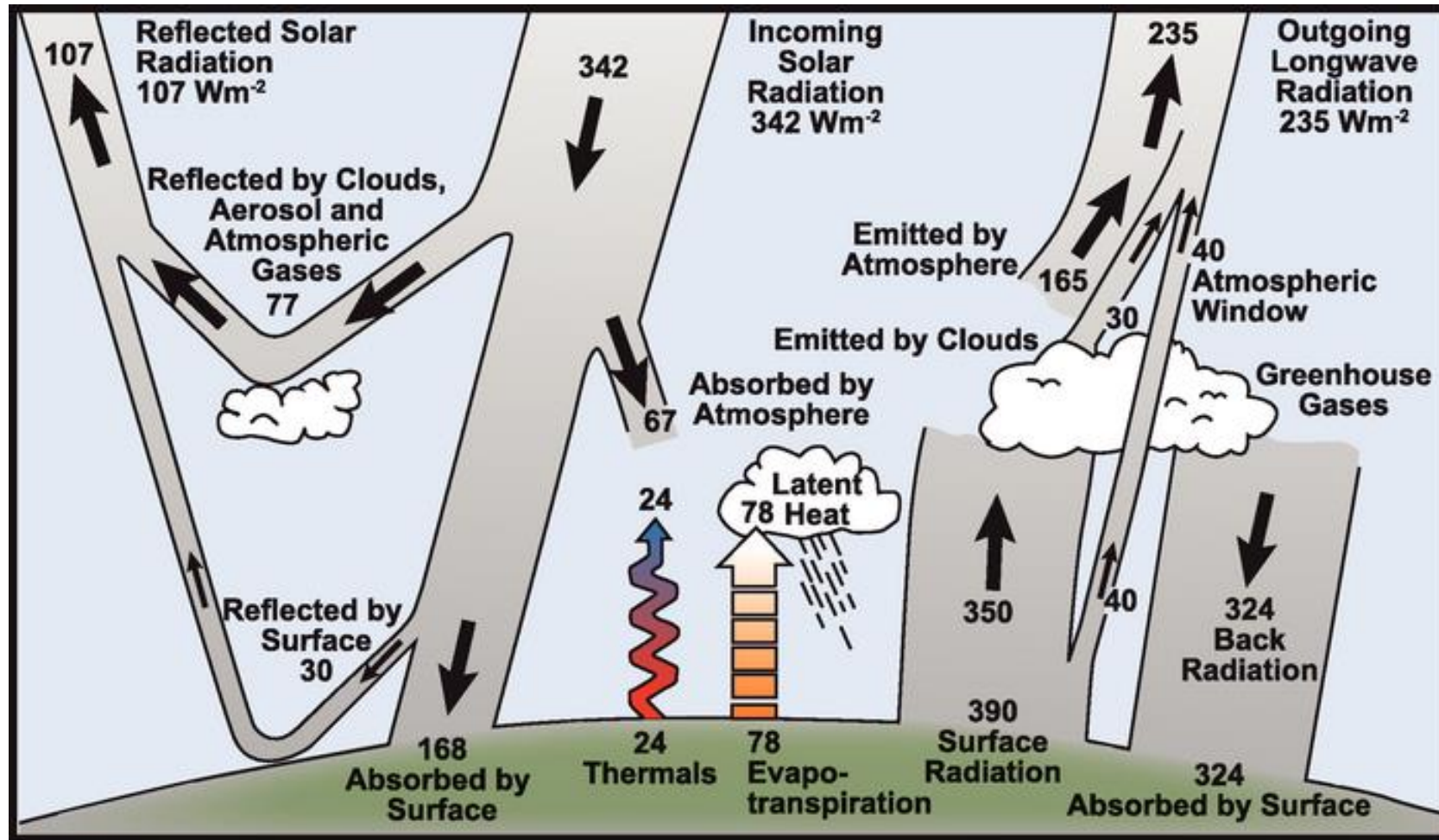
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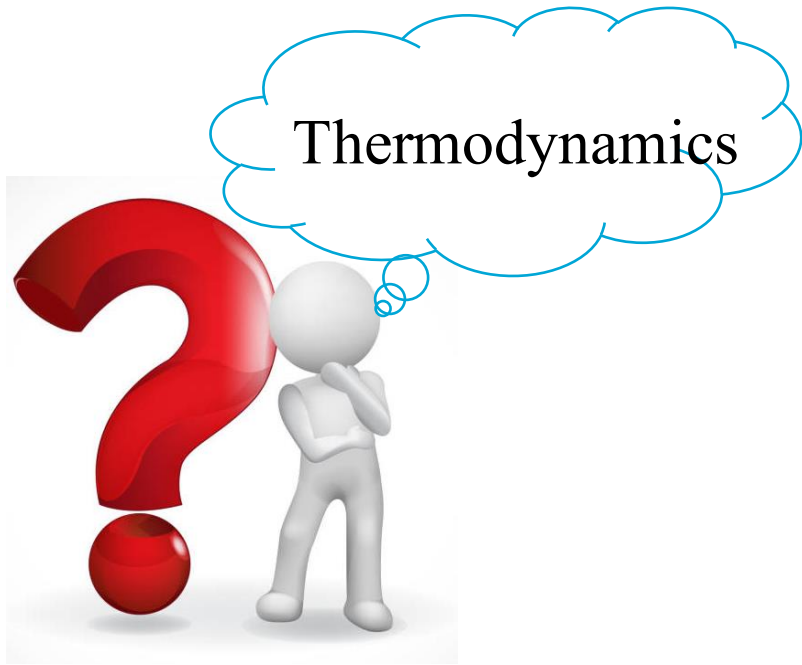
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Example: Radiation and climate change



What do we focus on?



Four thermodynamics laws:

- 0th law of thermodynamics (temperature) – Chapter 17
- Kinetic Theory of Gases (temperature) – Chapter 18
- 1st law of thermodynamics (energy) – Chapter 19
- 2nd law of thermodynamics (entropy) – Chapter 20
- 3rd law of thermodynamics (absolute 0 K) – Chapter 20

Structure of the lecture

- The Ideal Gas Law and the Molecular Interpretation of Temperature
- Distribution of Molecular Speeds
- Real Gas and Changes of Phase
- Vapor Pressure and Humidity
- Van der Waals Equation of State
- Mean Free Path
- Diffusion

Learning objectives

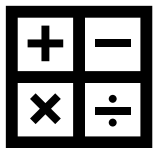
After today's lecture, you should be able to:



- Explain **molecular kinetic theory** for ideal gases, including, average kinetic energy, average speed and speed distribution.
- Explain the difference of ideal and **real gas**, using van der Waals theory



- Analyze **phase changes** for given substances, using phase diagrams.

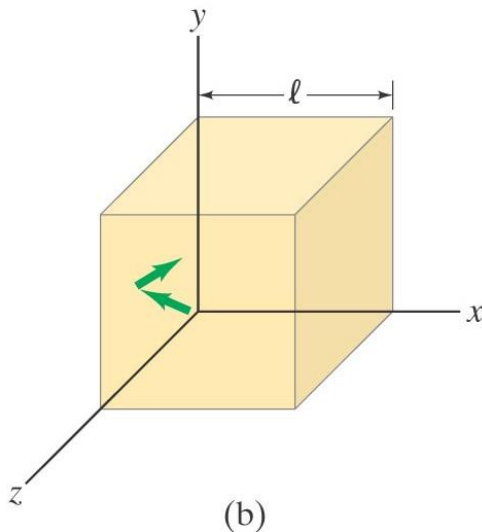
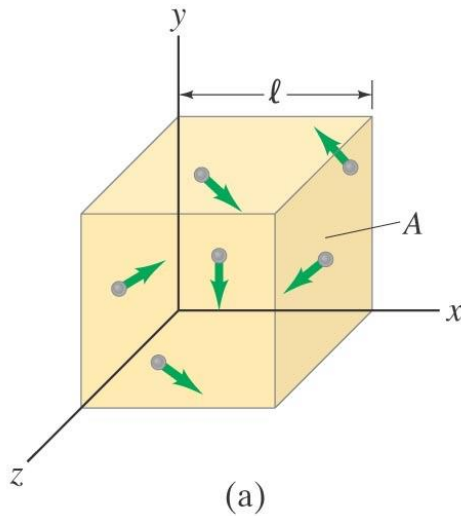


- Calculate **relative humidity** at given temperature.
- Calculate the **diffusion rate of molecules**

Prior knowledge

- Basic mechanics (e.g., *Newton's law*)
- Calculus (*differential and integral*)
- Statistics (*distribution, probability*)

18-1 Force per molecule



Pressure exerted on a wall of a container of gas is due to collisions of the molecules with the walls

one molecule striking wall (yz-plane):

$$\left\{ \begin{array}{l} \Delta(mv) = mv_x - (-mv_x) \\ \Delta t = \frac{2l}{v_x} \end{array} \right.$$



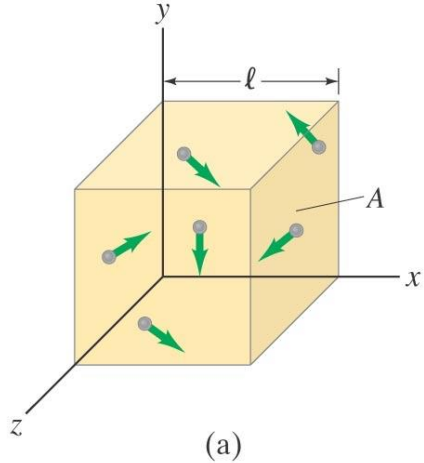
Newton's 2nd law:

$$F = \frac{\Delta(mv)}{\Delta t}$$

$$F = \frac{mv_x^2}{l}$$

= average force due to one molecule
(having many collisions with the wall)
this includes the effect of collisions
with other molecules

18-1 Average translational kinetic energy of molecules



$$F = \frac{m(v_{x,1}^2 + v_{x,2}^2 + \dots + v_{x,N}^2)}{l} = \frac{mN\overline{v_x^2}}{l}$$

With $v_{x,N}$ stands for the v_x of molecule N

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

random motion, no preference for certain direction

$$F = \frac{mN\overline{v^2}}{3l}$$

N very large, P constant

$$P = \frac{F}{A} = \frac{1}{3} \frac{Nm\overline{v^2}}{V}$$



$$PV = \frac{2}{3} N \left(\frac{1}{2} m\overline{v^2} \right) = \frac{2}{3} N\bar{K}$$

average translational kinetic energy

$$\bar{K} = \frac{3}{2} kT$$

$$PV = NkT$$

combine with ideal gas law

18-1 Root mean square speed

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

Mass of one molecule O₂ (molecular mass = 32u) is: $m(O_2) = (32)(1.66 \times 10^{-27}) = 5.3 \times 10^{-26} \text{ kg}$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{5.3 \times 10^{-26} \text{ kg}}} = 481 \text{ m/s}$$

Mass of one molecule He (molecular mass = 4u) is: $m(He) = (4)(1.66 \times 10^{-27}) = 6.6 \times 10^{-27} \text{ kg}$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{6.6 \times 10^{-27} \text{ kg}}} = 1357 \text{ m/s}$$

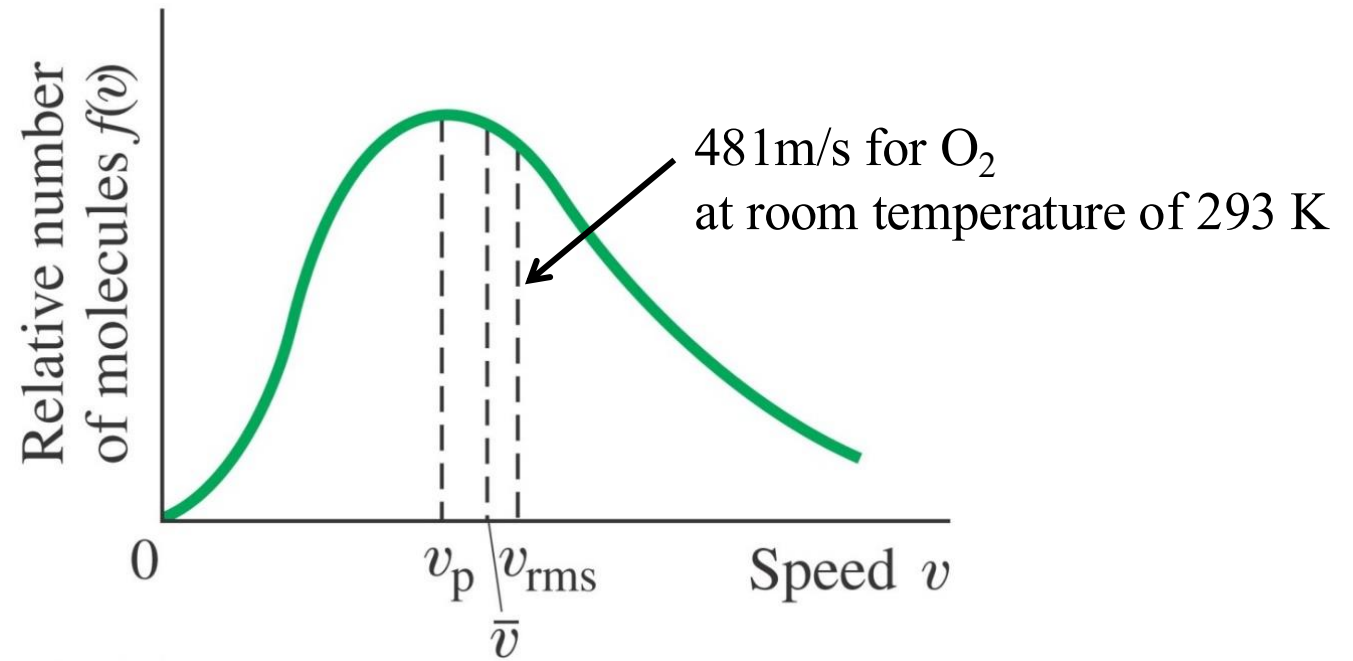
18-2 Maxwell distribution

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}}$$

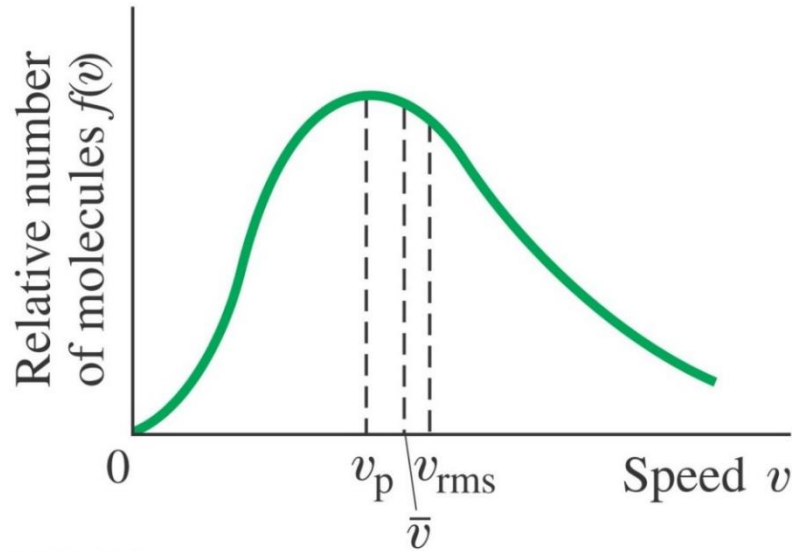
$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

$$\bar{v} = \frac{\int_0^{\infty} v f(v) dv}{N} \quad \bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$\frac{df(v)}{dv} = 0 \longrightarrow v_p = \sqrt{\frac{2kT}{m}}$$

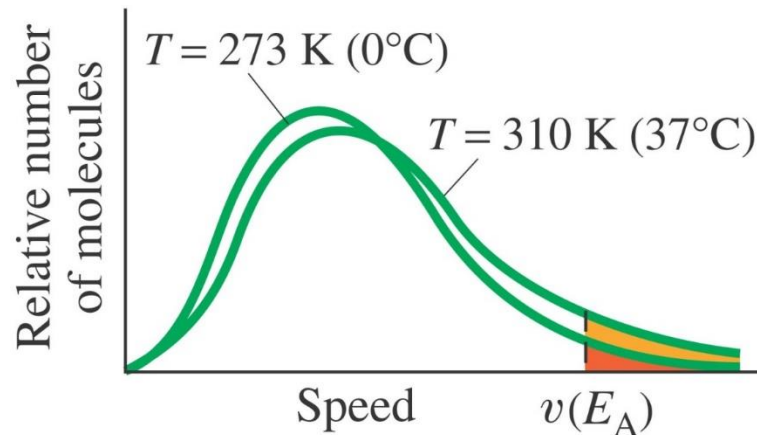


18-2 Temperature dependence of speed distribution



$$f(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}}$$

only dependent on T !



Chemical reactions take place more rapidly as T increases! (E_A activation energy)

18-2 Example - maxwell distribution of speeds

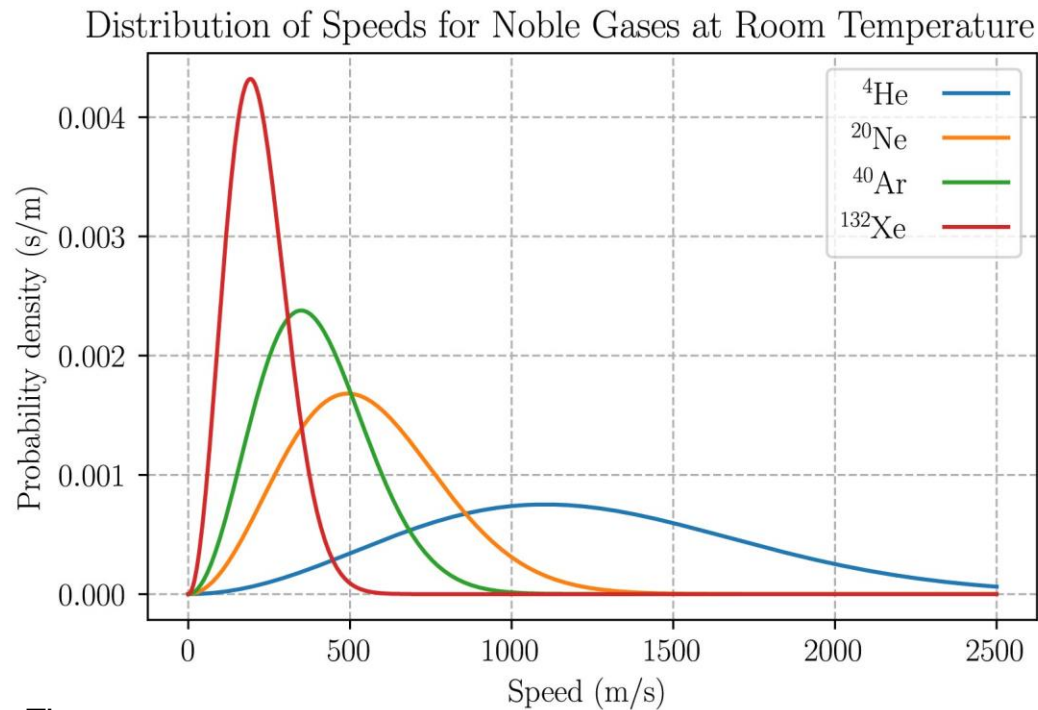
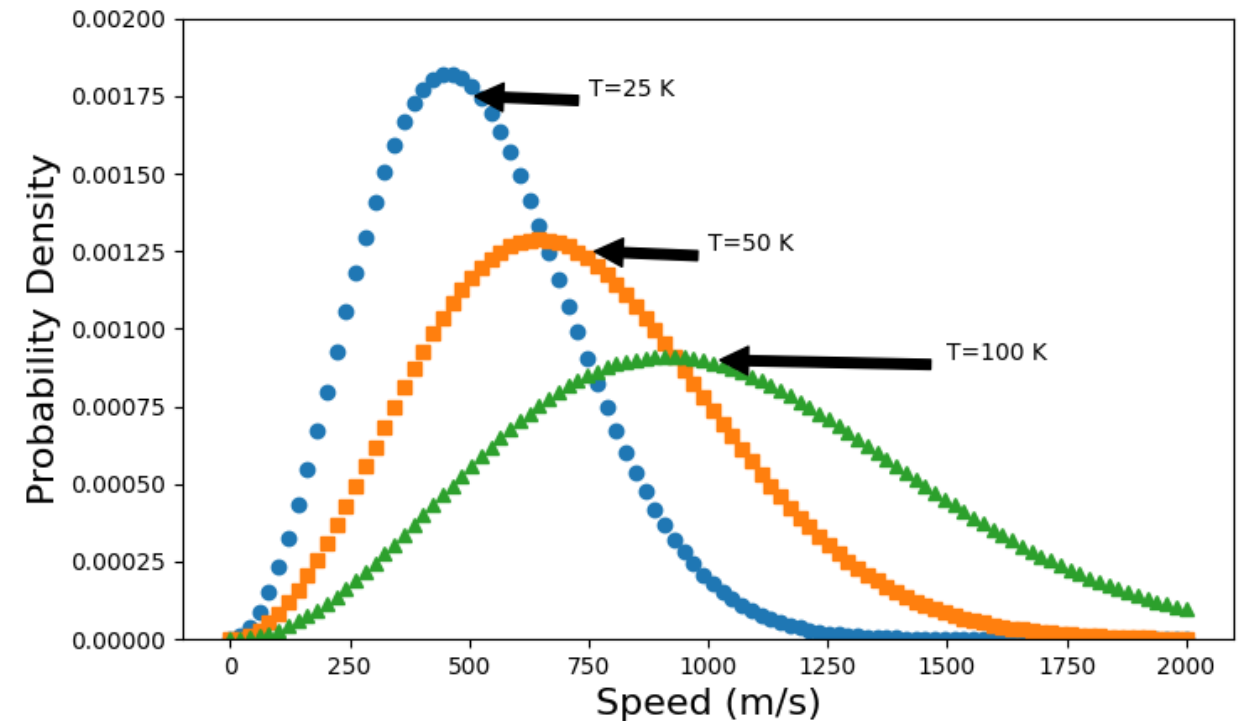


Figure source:

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Distribution of speeds for H_2 at different temperatures

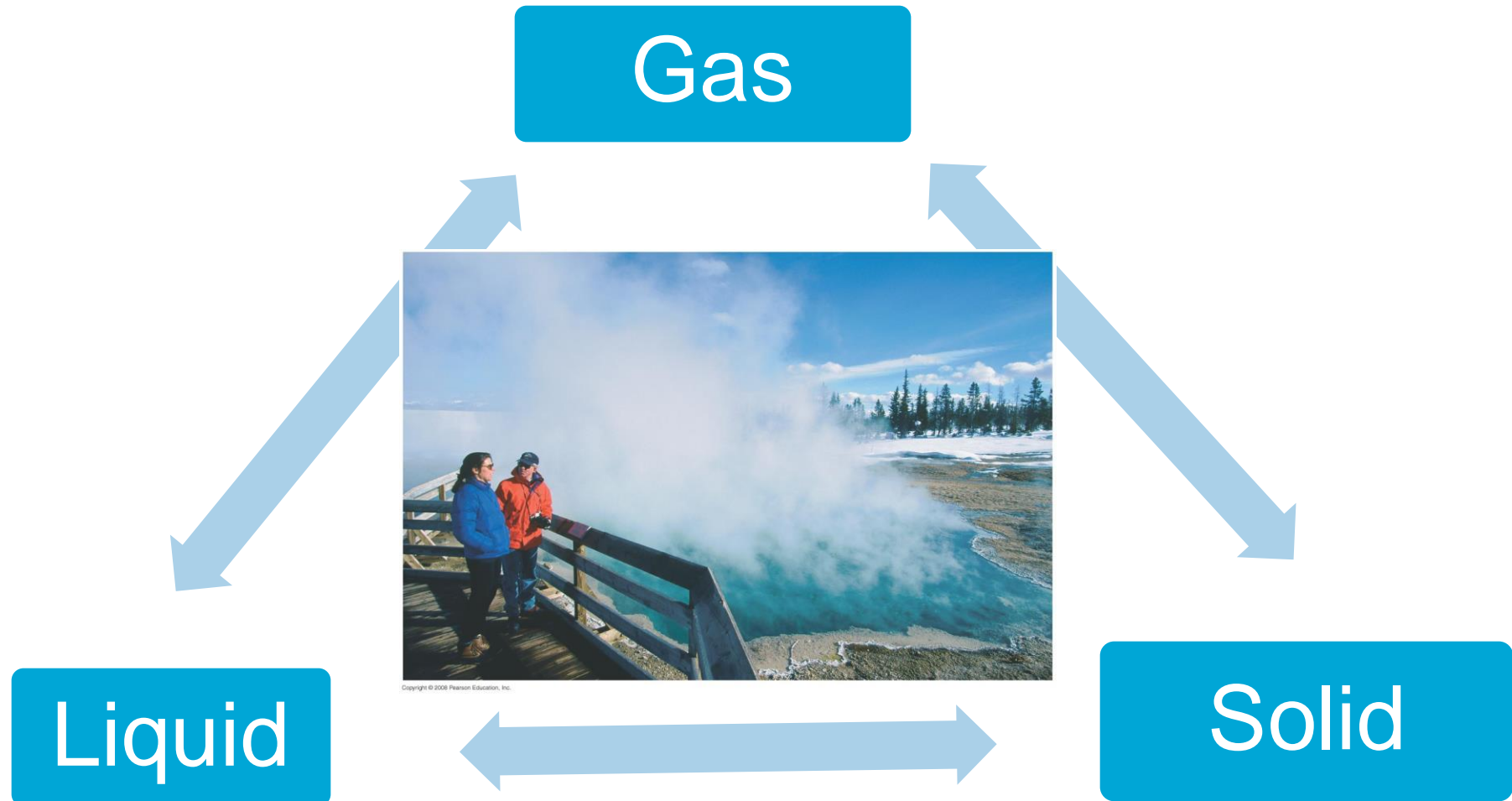


Exercise

In outer space, the density of matter is about one atom per cm^3 (mainly hydrogen *atoms*). The temperature is about 2.7 K.

- What is the rms speed of the hydrogen atoms?
- What is the pressure in the atmosphere?

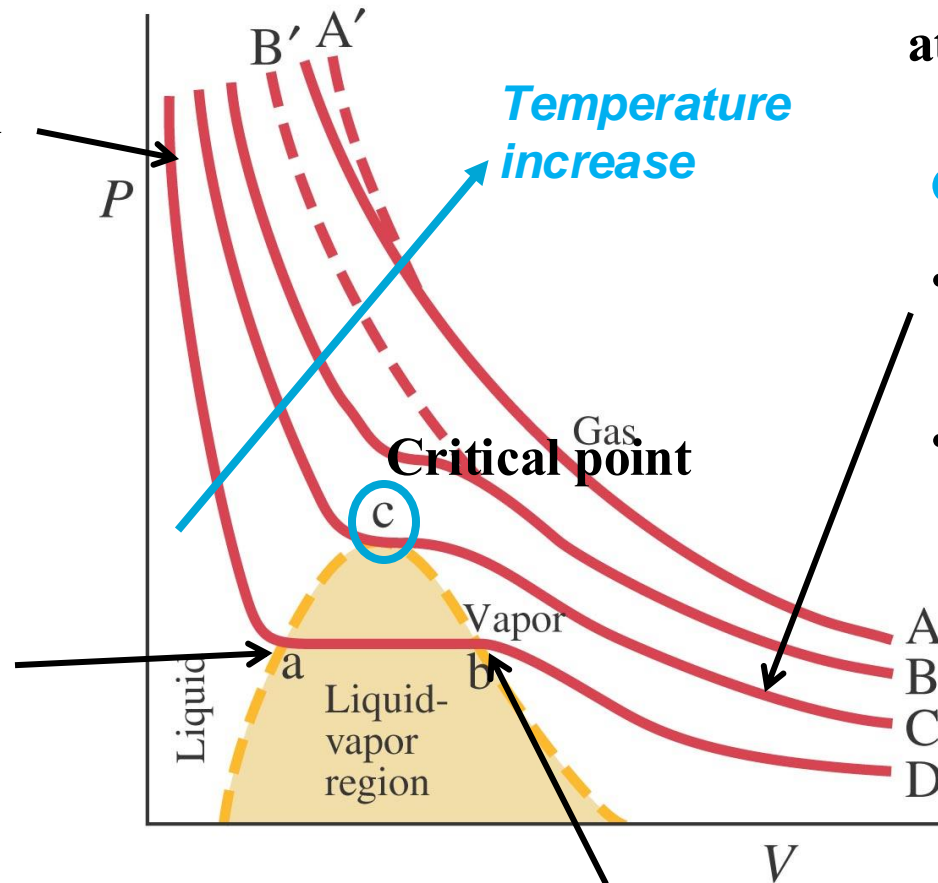
18-3 Phase change



18-3 P-V diagram

Steep rise as liquids are nearly incompressible

All of the substance has become liquid



- Dashed lines: ideal gas behavior: $PV = NkT$;
- Solid lines: real gas behavior driven by **attractive forces** (see 18-6 for details);

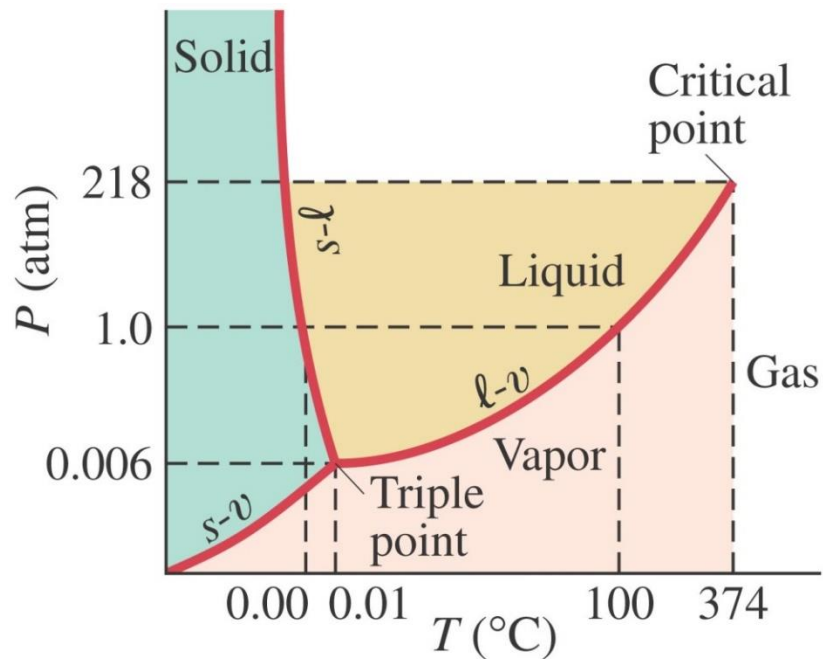
Critical temperature (T_c):

- $< T_c$: a gas changes to liquid with sufficient high pressure;
- $> T_c$: no phase change.

Substance	Critical temperature [K]	Critical pressure [atm]
Water	647	218
Nitrogen	126	33.5
Hydrogen	33.3	12.8

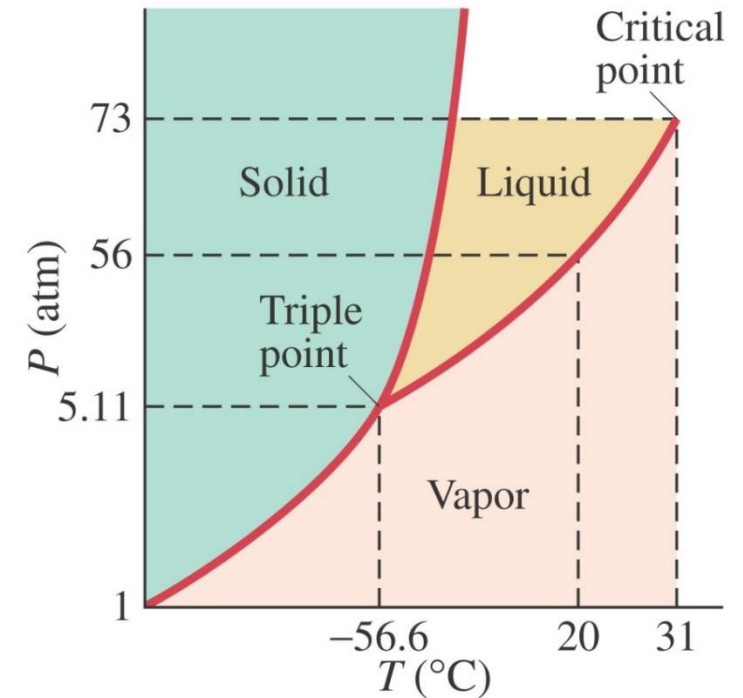
18-3 P-T diagram

P-T diagram for water



- Curve (ℓ - u): liquid and vapour phase are in equilibrium (boiling point vs. pressure)
- Curve (s - ℓ): solid and liquid phase are in equilibrium (freezing point)
- Curve (s - u): Sublimation point
- Triple point: three phases coexist in equilibrium (unique value of P and T)
- Low pressure (< 0.006 atm): sublimation

P-T diagram for CO₂



18-4 Vapor Pressure and Humidity

- Equilibrium exists, and saturation occurs
- The pressure of the vapour when saturation occurs is called saturated vapor pressure

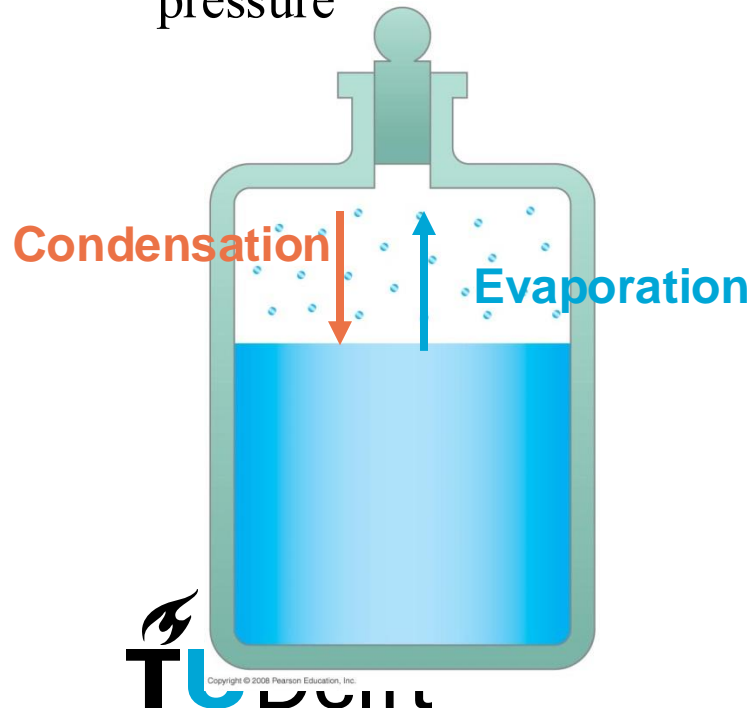


TABLE 18–2 Saturated Vapor Pressure of Water

Temp- erature (°C)	Saturated Vapor Pressure	
	torr (= mm-Hg)	Pa (= N/m ²)
–50	0.030	4.0
–10	1.95	2.60×10^2
0	4.58	6.11×10^2
5	6.54	8.72×10^2
10	9.21	1.23×10^3
15	12.8	1.71×10^3
20	17.5	2.33×10^3
25	23.8	3.17×10^3
30	31.8	4.24×10^3
40	55.3	7.37×10^3
50	92.5	1.23×10^4
60	149	1.99×10^4
70 [†]	234	3.12×10^4
80	355	4.73×10^4
90	526	7.01×10^4
100 [‡]	760	1.01×10^5
120	1489	1.99×10^5
150	3570	4.76×10^5

[†]Boiling point on summit of Mt. Everest.

[‡]Boiling point at sea level.

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depends on T , not on V (when air is there or not)



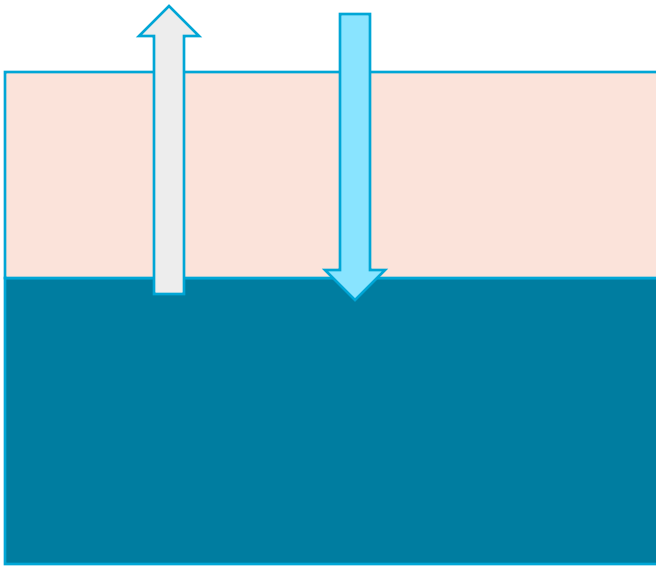
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Boiling: when saturated vapour pressure inside bubble equals external pressure

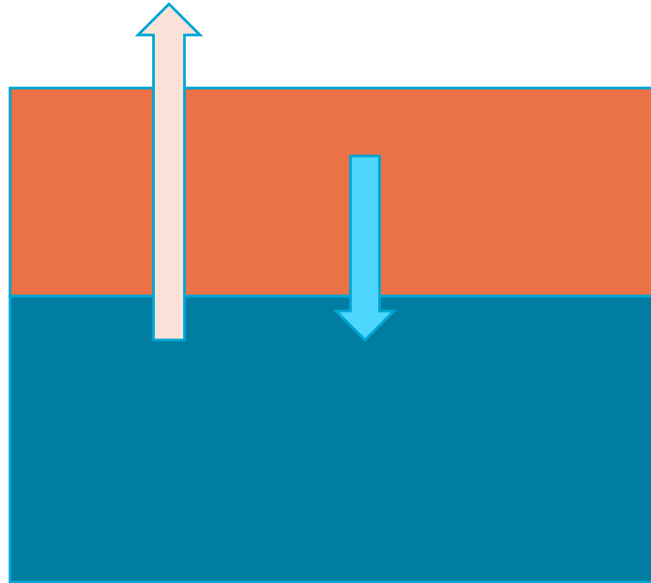
At top of Mt. Everest air pressure is 1/3 of that at sea level. Then at what temperature water boils? **70 °C**

Concept of relative humidity

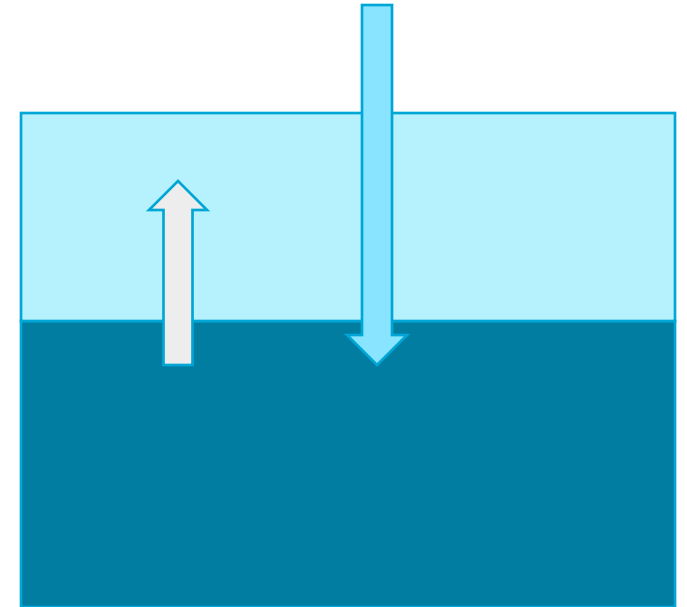
$$\text{relative humidity} = \frac{\text{partial pressure of water}}{\text{saturated vapor pressure}}$$



Equilibrium: saturation reached.
Partial pressure = saturated
vapour pressure
Relative humidity = 100%



Warm air: more evaporation



Cold air: more condensation

18-4 Vapor Pressure and Humidity

$$\text{relative humidity} = \frac{\text{partial pressure of water}}{\text{saturated vapor pressure}}$$

Example: hot day, $T = 30\text{ }^{\circ}\text{C}$ and partial pressure of water is 21.0 torr

then relative humidity is $21.0/31.8 \times 100\% = 66\%$

when T falls to $20\text{ }^{\circ}\text{C}$ (saturated vapor pressure = 17.5 torr), relative humidity $> 100\%$ (air is *supersaturated*) \rightarrow excess water condenses as dew, fog or rain

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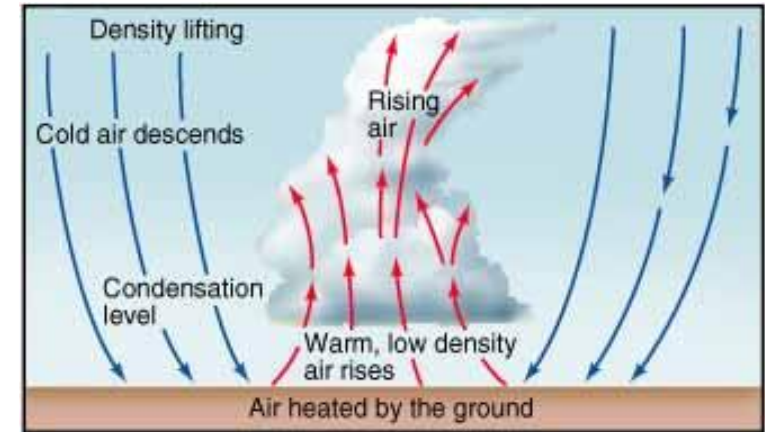
[†]Boiling point on summit of Mt. Everest.

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18-4 Supersaturation and dew point

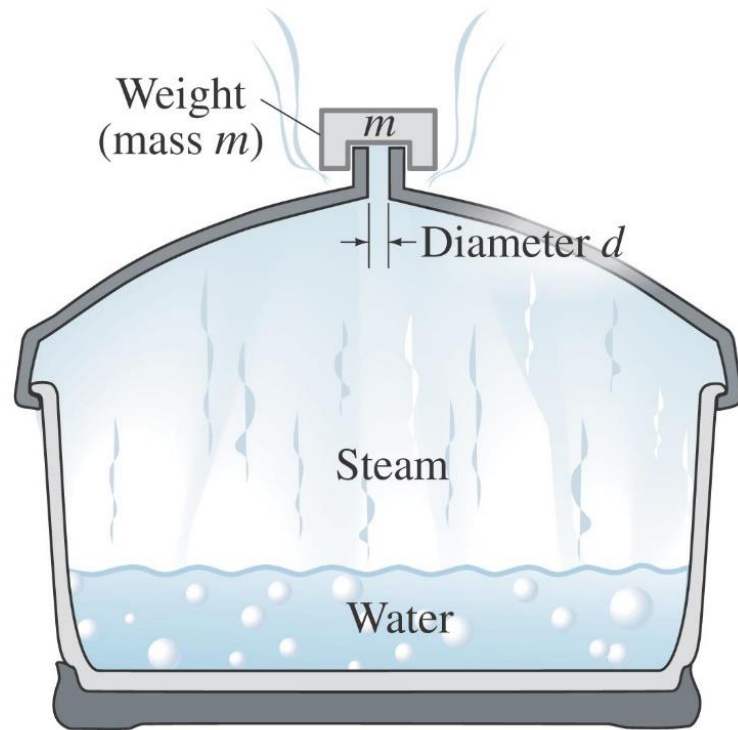
- If the partial pressure of water exceeds the saturated vapour pressure, the air is **supersaturated**;
- This can occur when temperature reduces, e.g., lift air;
- or partial pressure increase, e.g., water vapour emission from engine exhaust;
- **Dew point**: the point where the partial pressure of water reaches the saturated vapour pressure when the air is cooled.



Exercise

What is the mass of water in a closed room of 5.0 m x 3.0 m x 2.5 m when the temperature is 25 °C and the relative humidity is 65 %?

Problem 33 pressure cooker

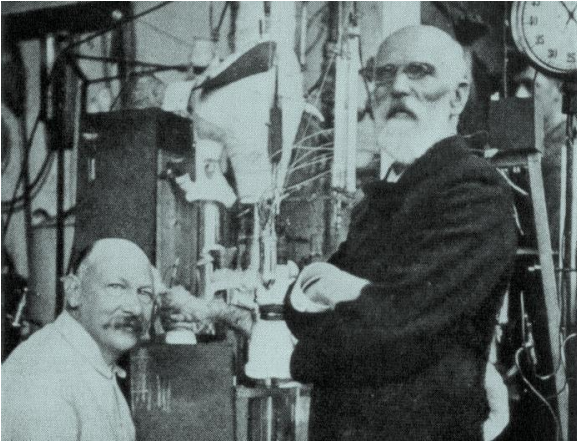


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- A pressure cooker is a sealed pot designed to cook food with the steam produced by boiling water above $100\text{ }^{\circ}\text{C}$.
- It uses a weight of mass m to allow steam to escape at a certain pressure through a small hole in the lid. The diameter of the hole is d equal to 3.0 mm .

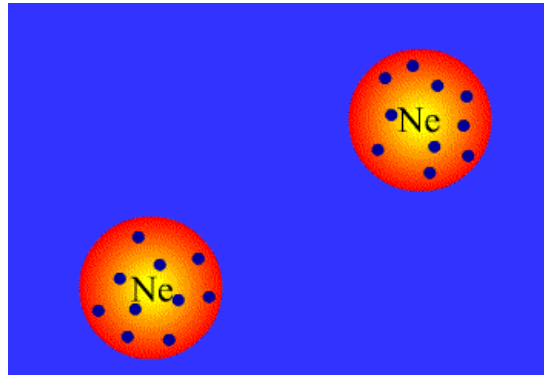
What should m be in order to cook food at $120\text{ }^{\circ}\text{C}$?
(assume atmospheric pressure outside the cooker is 1 atm)

18-6 Van der Waals Equation of State



Nobel prize in physics 1910

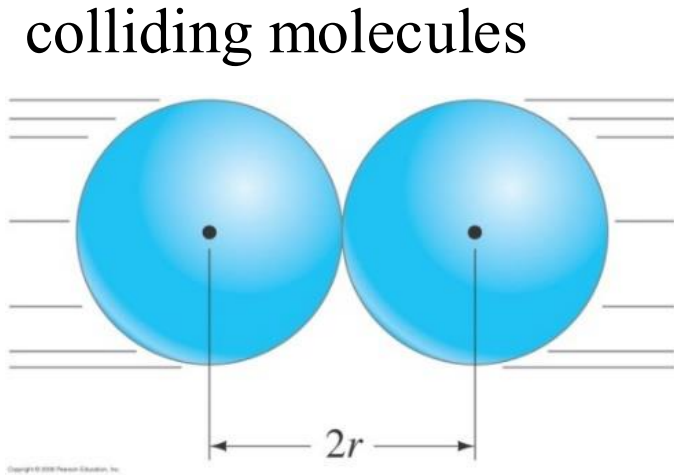
[Van der Waals forces](#)



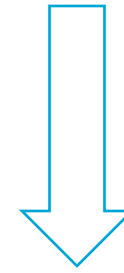
Animation from:
<http://www.chm.bris.ac.uk/webprojects2003/swinerd/forces/forces.htm>

- Based on kinetic theory
- Non-negligible volume of molecules
- Range of attractive forces larger than size of molecules
- The actual volume in which the molecules can move is smaller than the volume of container.

18-6 Clausius equation of state--effects of molecule size



$$PV = nRT$$



b represents the
unavailable volume
per mole of gas

$$P(V - nb) = nRT$$

$$P \left(\frac{V}{n} - b \right) = RT$$

$P_{real} < P_{ideal}$ for given
temperature
and volume

18-6 Van der Waals equation of state—effects of attractive force

- Molecules towards wall are slowed down
- The corresponding reduced pressure is proportional to density of molecules in layer of gas at the surface (and to density in next layer)
- Actual forces exerted on the wall is less due to attractive forces;
- We expect the pressure to be reduced is proportional to the density squared $(n/V)^2$

$$P = \frac{nRT}{V - nb} - \frac{a}{(V/n)^2}$$

Constant a, b differ per gas

$$T_{cr} = \frac{8a}{27bR} \quad P_{cr} = \frac{a}{27b^2}$$

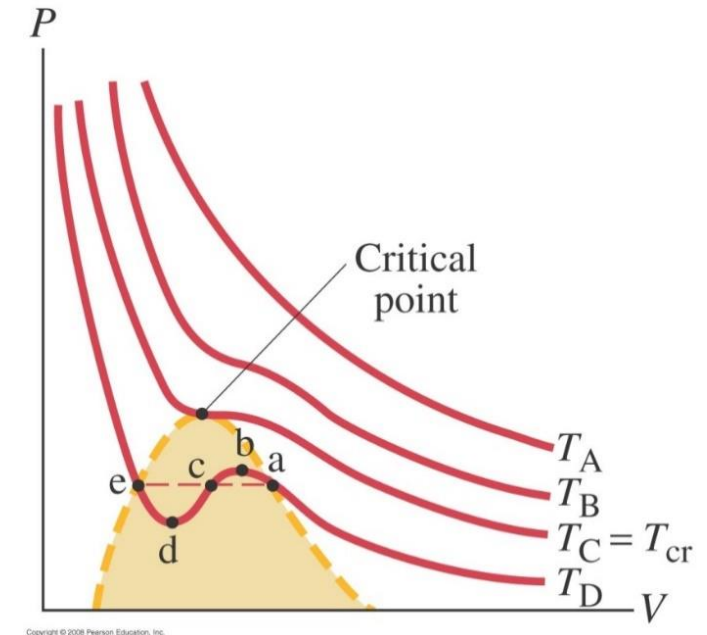
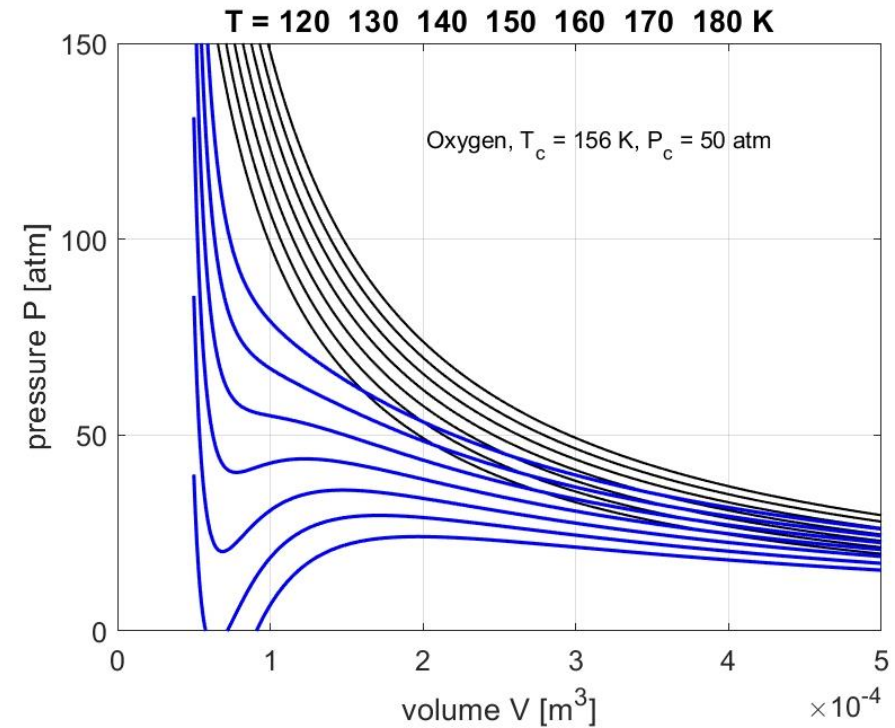
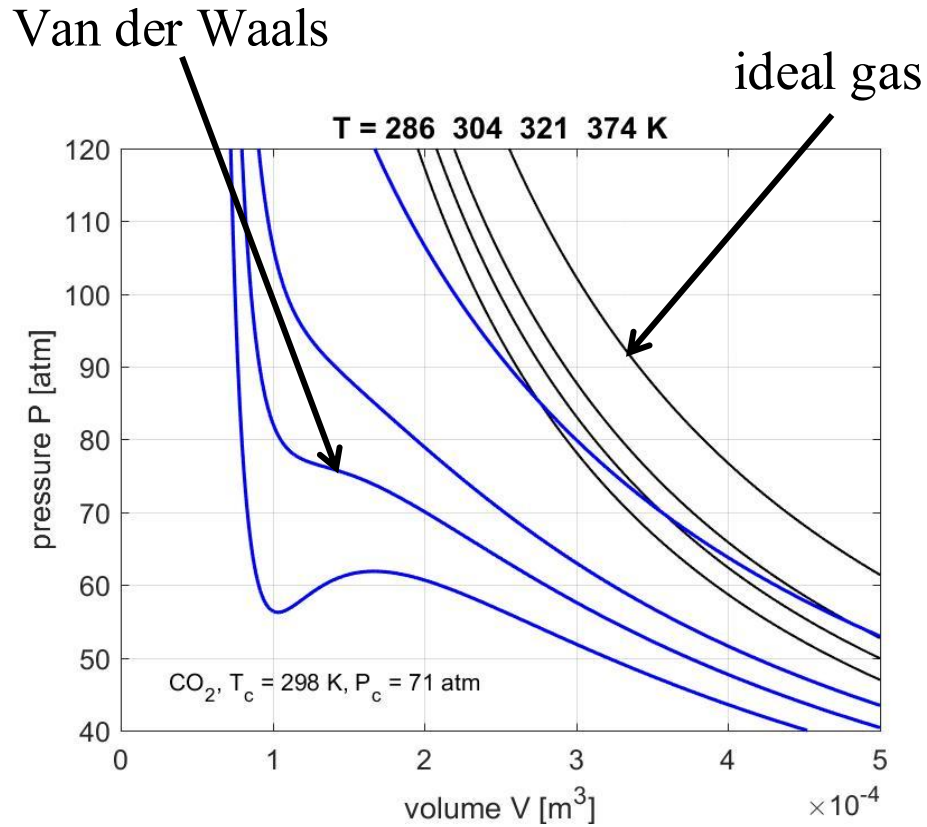


Figure 18-11 PV diagram for van der Waals gas. Points b & d are artifacts

18-6 Van der Waals Equation of State—comparison



18-7 Mean Free Path

---average distance molecule travels between collisions

- If molecules were true point particles, they would never collide with one another.
- **Mean free path distance** is the average distance a molecule travels between collisions.
- Greater molecule, greater air density \rightarrow shorter mean free path distance

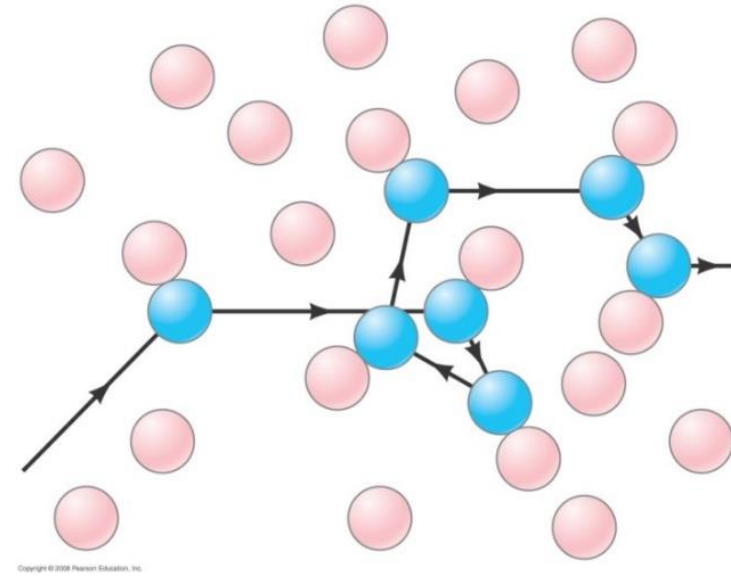
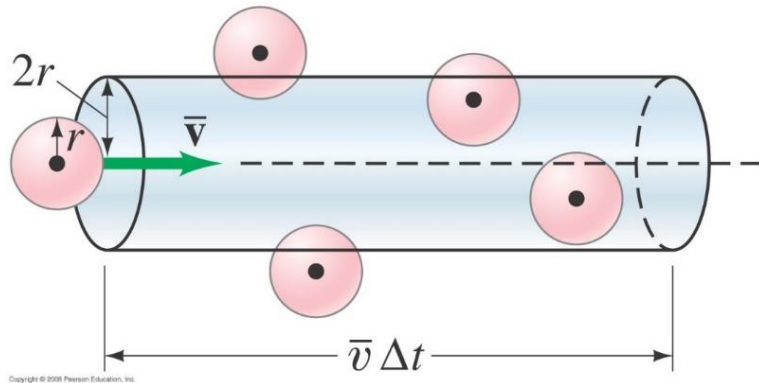


Figure 18-12 Zigzag path of a molecule colliding with other molecules.

18-7 Mean Free Path

---average distance molecule travels between collisions



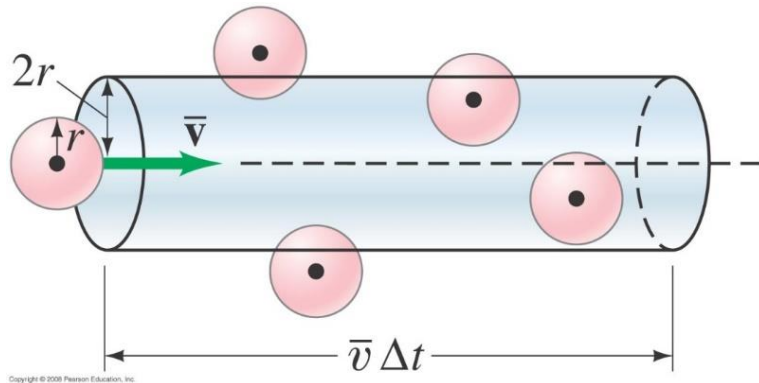
- Molecules are hard spheres with radius r ;
- Dashed line: molecule moves from left to right with speed \bar{v} without collision;
- Assuming the other molecules are still;
- Concentrations of molecules (#/volume) are N/V ;
- Number of Collision = concentration * volume

Mean free distance:
$$l_M = \frac{\bar{v} \Delta t}{\pi (2r)^2 \bar{v} \Delta t (N/V)} = \frac{1}{4\pi r^2 (N/V)}$$

We expect mean free path to be inversely proportional to density N/V and size ($\sim r^2$) of the molecules

18-7 Mean Free Path

---average distance molecule travels between collisions



- Assuming the other molecules are still

$$l_M = \frac{\bar{v} \Delta t}{\pi (2r)^2 \bar{v} \Delta t (N/V)}$$

Not true!

- Relative speed matters:

$$v_{rel} = \sqrt{2} \bar{v}$$

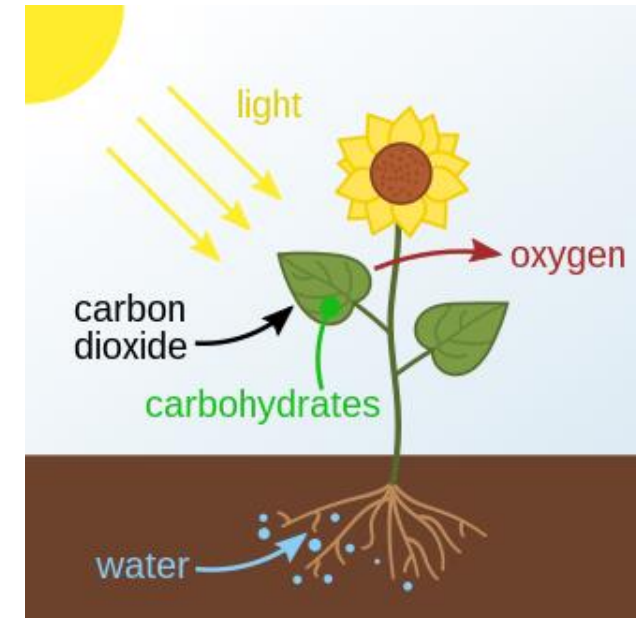
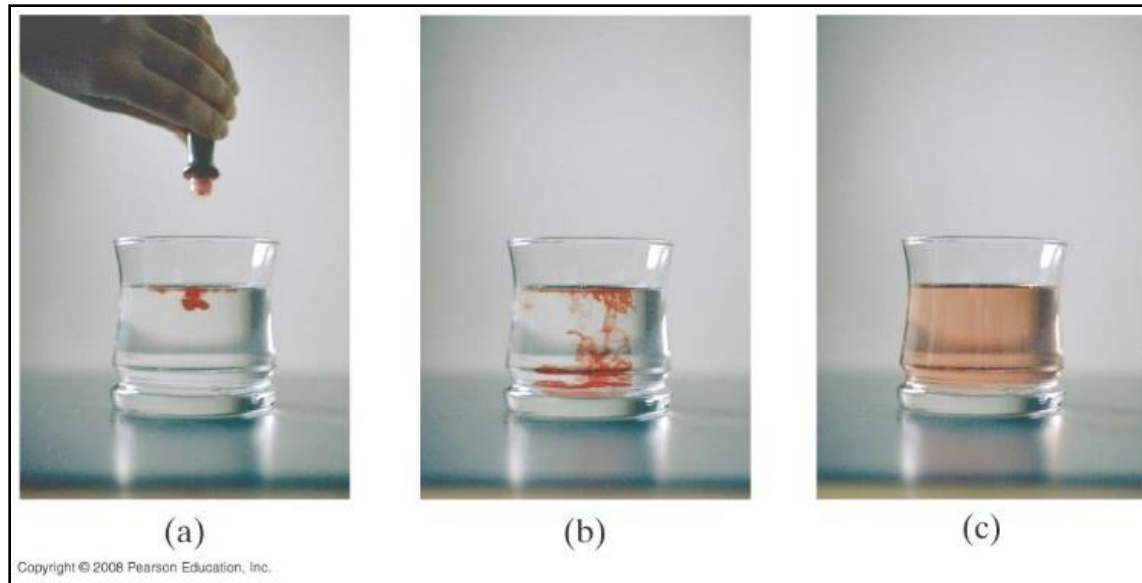
Mean free distance:

$$l_m = \frac{1}{4\pi\sqrt{2}r^2(N/V)}$$

Example 18-8 Mean free path of air molecules at STP

Estimate the mean free path of air molecules at STP, standard temperature and pressure (0°C, 1 atm). The diameter of O₂ and N₂ molecules is about 3×10^{-10} m.

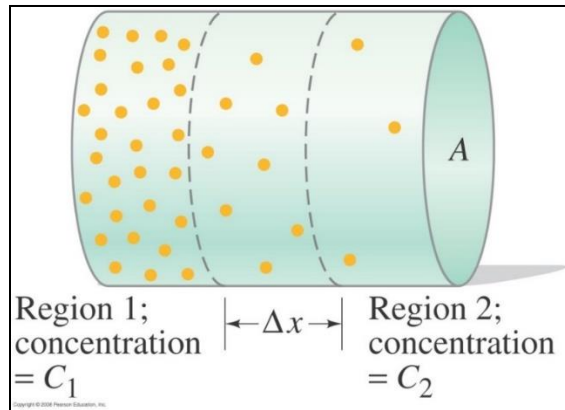
18-8 Diffusion



- Takes place because of the random motion of molecules
- Diffusion depends on concentrations ($\text{\#}/\text{mol}$; $\text{\#}/\text{m}^3$)
- Diffusing direction: high concentration region \rightarrow low concentration region

18-8 Fick's law

- often convection (moving air currents) plays a greater role than diffusion
- diffusion can be understood on the basis of kinetic theory



- more molecules cross into central region from region 1 than from region 2 →
- net flow of molecules from left to right

TABLE 18-3 Diffusion Constants, D (20°C, 1 atm)

Diffusing Molecules	Medium	D (m ² /s)
H ₂	Air	6.3×10^{-5}
O ₂	Air	1.8×10^{-5}
O ₂	Water	100×10^{-11}
Blood hemoglobin	Water	6.9×10^{-11}
Glycine (an amino acid)	Water	95×10^{-11}
DNA (mass 6×10^6 u)	Water	0.13×10^{-11}

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$$\begin{array}{c}
 \text{Rate of} \\
 \text{diffusion in} \\
 \text{mol/s}
 \end{array}
 \nearrow J = DA \frac{C_1 - C_2}{\Delta x}
 \begin{array}{c}
 \nearrow D \\
 \nwarrow A
 \end{array}
 \begin{array}{c}
 \text{Diffusion} \\
 \text{factor}
 \end{array}
 \begin{array}{c}
 \nwarrow C_1 - C_2 \\
 \nearrow \Delta x
 \end{array}
 \begin{array}{c}
 \text{Concentration} \\
 \text{gradient in mol/m}^4
 \end{array}
 \rightarrow \boxed{J = DA \frac{dC}{dx}}$$

Wrap up: learning objectives

- Explain **molecular kinetic theory** for ideal gases, including, average kinetic energy, average speed and speed distribution.

$$\bar{K} = \frac{3}{2} kT$$

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}}$$

- Explain the **real gas behaviors**, using van der Waals theory

$$P = \frac{nRT}{V - nb} - \frac{a}{(V/n)^2}$$

- Analyze **phase changes** for given substances, using phase diagrams.

- Calculate **relative humidity** at given temperature. $RH = \frac{\text{partial pressure of water}}{\text{saturated vapor pressure}}$

- Calculate the **diffusion rate of molecules**

$$J = DA \frac{dC}{dx}$$

Summary

- **Translational kinetic energy** of molecules in random motion in ideal gas is proportional to **absolute temperature**;
- The molecular speed distribution within ideal gas is defined by **Maxwell distribution**;
- **Real gas behavior** occurs at high pressure and/or near the liquefaction point driven by attractive forces;
- **Phase changes**: (1) Critical temperature; (2) Triple point;
- **Humidity**: (1) Evaporation; (2) Saturated vapor pressure; (3) Partial pressure; (4) Relative humidity;
- **Van der Waals equation of state**: microscopic view of real gas behaviors;
- **Mean free path**: average distance a molecule travels between collision;
- **Diffusion** due to random movement of molecules between different concentrations per substance.

Thank you for your attention!

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