# Physics 5D: Heat, Thermo, Kinetics

# Ch 18. Kinetic Theory of Gases

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Monday, October 7, 13

# Physics 5D: Heat, Thermo, Kinetics

## Homework 2 and the slides from this Lecture 2 are posted at
### http://physics.ucsc.edu/~joel/Phys5D

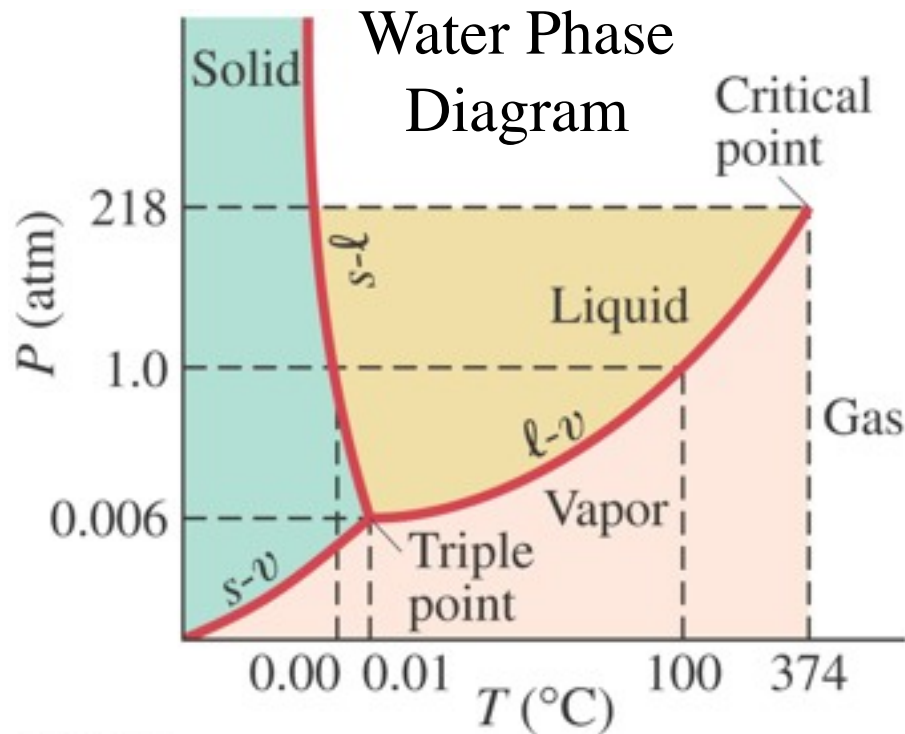## The solutions to Homework 1 will be posted after this lecture.

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# Real Gases and Changes of Phase

A *PT* diagram is called a **phase diagram**; it shows all three phases of matter. The solid-liquid transition is **melting** or **freezing**; the liquid-vapor one is **boiling** or **condensing**; and the solid-vapor one is **sublimation.**
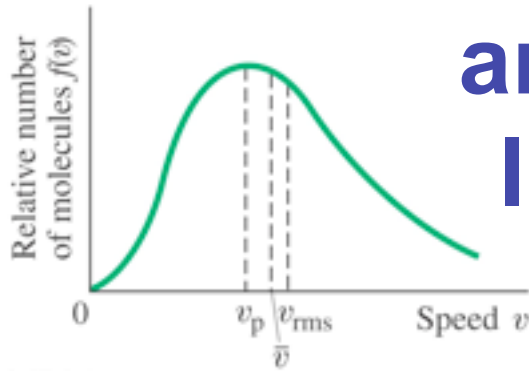


Water Phase Diagram

The **Triple point** is the only point where all three phases can coexist in **equilibrium.**

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# Real Gases and Changes of Phase

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Water Phase Diagram

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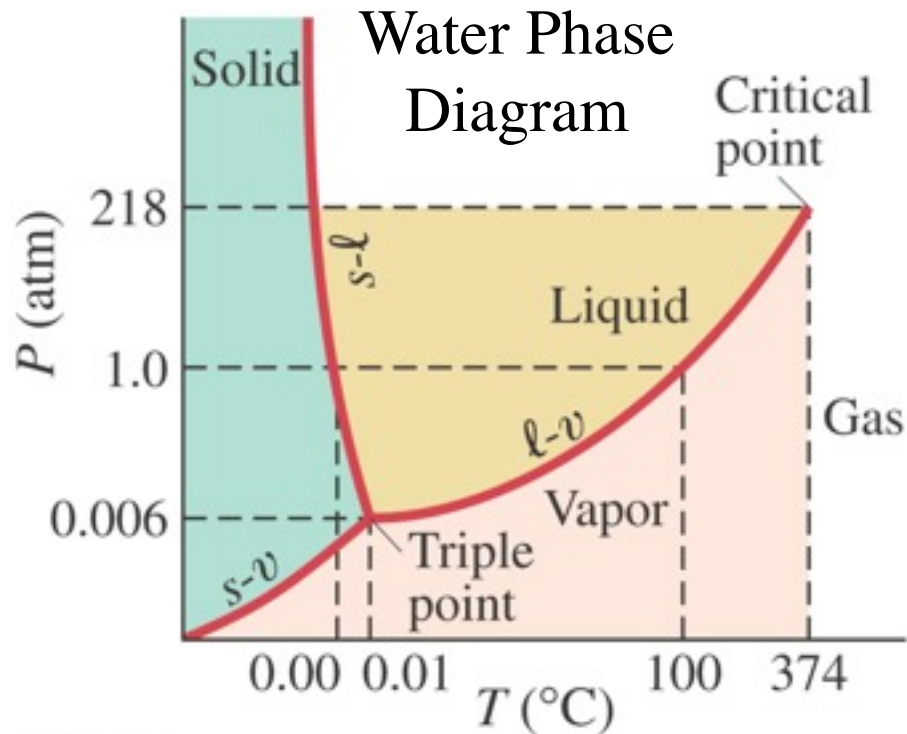
# 18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

**Assumptions of kinetic theory:**

• **large number of molecules, moving in random directions with a variety of speeds**

• **molecules are far apart, on average**

• **molecules obey laws of classical mechanics and interact only when colliding**

• **collisions are perfectly elastic**

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# A superball is thrown straight at a wall and bounces straight back. The magnitude of the momentum transferred to the wall is

- A. equal to the original momentum of the superball.

- B. twice the original momentum of the superball.

- C. zero.

- D. none of the above.

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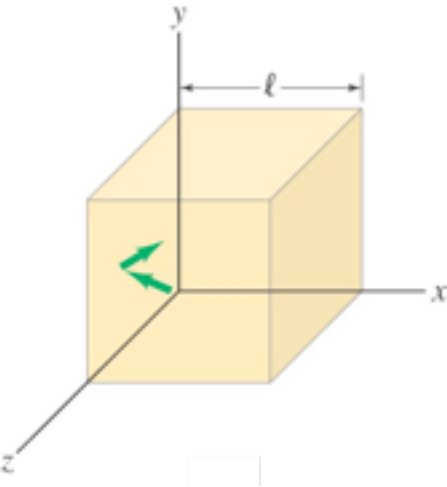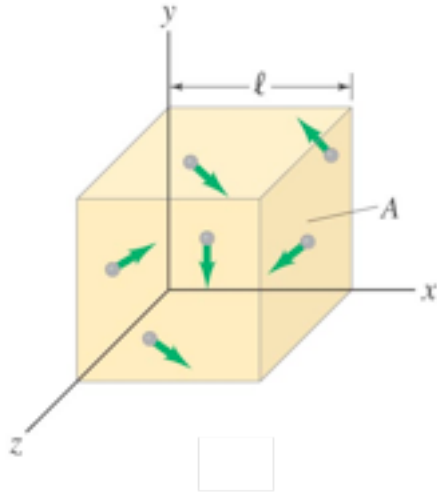
- A. equal to the original momentum of the superball.
- B. twice the original momentum of the superball.
- C. zero.
- D. none of the above.

**The superball's change in momentum is 2p, so the wall's must be -2p by momentum conservation: 2p - 2p = 0.**

# 18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

Pressure P = Force/Area = NkT/V .

The **force** exerted on the wall by the collisions of one molecule is

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}.$$

Then the force due to **all** $N$ molecules colliding with that wall is

$$F = \frac{m}{\ell} N \overline{v_x^2}.$$

**Daniel Bernoulli (1700-1782)**

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# 18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

The **averages of the squares** of the speeds in all three directions are equal: $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \overline{v^2}/3$, where $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$. Therefore

$$F = \frac{m}{\ell} N \overline{v_x^2}$$ implies that $$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3}.$$

So the **pressure** $P \equiv F/A$ is $$P = \frac{1}{3} \frac{N m \overline{v^2}}{V}.$$

Rewriting,

$$PV = \tfrac{2}{3} N \left( \tfrac{1}{2} m \overline{v^2} \right).$$

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# 18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

We just showed that $PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right)$,

but the Ideal Gas Law says $PV = NkT$, so

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

The average **translational kinetic energy** $\overline{K}$ of the molecules in an ideal gas is directly proportional to the **temperature** of the gas.

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**Suppose the speed of every molecule in a gas were tripled. What would happen to the Kelvin temperature of the gas?**

- A. It would triple.

- B. It would go up by $3^{1/2}$.

- C. It would go up by a factor of 9.

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$$\overline{K} \;=\; \tfrac{1}{2} m \overline{v^2} \;=\; \tfrac{3}{2} kT.$$

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# 18-1 The Ideal Gas Law and the Molecular Interpretation of Temperature

**We can now calculate the root mean square speed** of molecules in a gas as a function of temperature**:**

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

**since**

$$\overline{K} = \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT.$$

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# The air in this room is a mixture of mostly nitrogen and oxygen molecules. Which of the following statements is true?

- A. The average speeds of the nitrogen and oxygen molecules are equal.

- B. The average magnitudes of momentum of the nitrogen and oxygen molecules are equal.

- C. The average kinetic energies of the nitrogen and oxygen molecules are equal.

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# Example 18-2: Speeds of air molecules.

**What is the rms speed of air molecules ($O_2$ and $N_2$) at room temperature (20°C)?**

A. Oxygen: 480 m/s. Nitrogen: 510 m/s

B. Nitrogen: 480 m/s. Oxygen: 510 m/s

C. Oxygen: 500 m/s. Nitrogen: 500 m/s.

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**Example 18-2: Speeds of air molecules.**

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A. Oxygen: 480 m/s. Nitrogen: 510 m/s

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C. Oxygen: 500 m/s. Nitrogen: 500 m/s.

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

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## Conceptual Example 18-3: Less gas in the tank.

A tank of helium is used to fill some balloons. As each balloon is filled, the number of helium atoms remaining in the tank decreases. How does this affect the rms speed of molecules remaining in the tank?

A. Increases.

B. Decreases.

C. Stays the same.

# Conceptual Example 18-3: Less gas in the tank.

A tank of helium is used to fill some balloons. As each balloon is filled, the number of helium atoms remaining in the tank decreases. How does this affect the rms speed of molecules remaining in the tank?

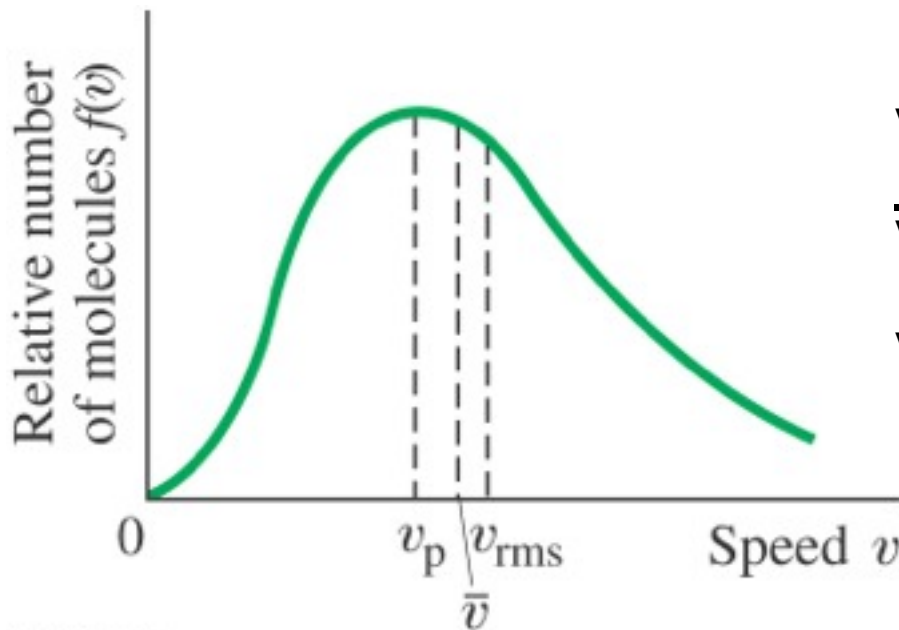A. Increases.

B. Decreases.

C. Stays the same.

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

**(assuming the temperature of the tank stays the same)**

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# 18-2 Distribution of Molecular Speeds

**The molecules in a gas will not all have the same speed; their distribution of speeds is called the Maxwell distribution:**

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

$v_p$ = most probable speed = mode

$\bar{v}$ = average speed

$v_{rms} = (\bar{v^2})^{1/2}$ = root-mean-square speed

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# 18-2 Distribution of Molecular Speeds

The Maxwell distribution depends only on the absolute (Kelvin) temperature. This figure shows distributions for two different temperatures; at the higher temperature, the whole curve is shifted to the right.

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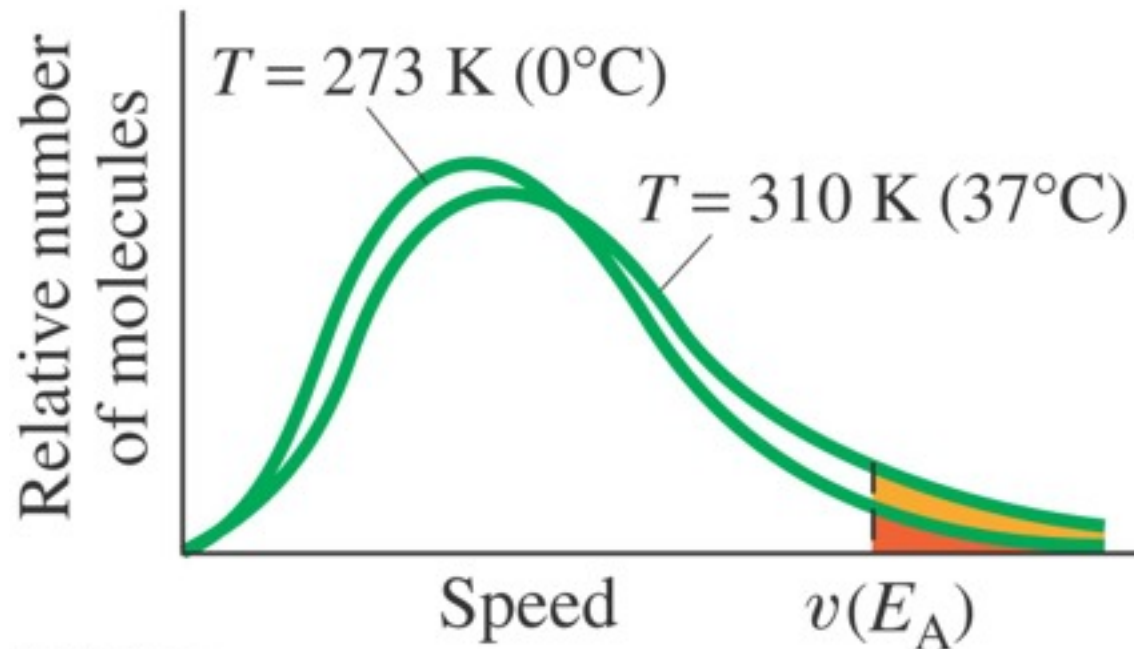
# 18-3 Real Gases and Changes of Phase

The isotherm curves here represent the behavior of the gas at different **temperatures**. The **cooler** it gets, the **further** the gas is from ideal.
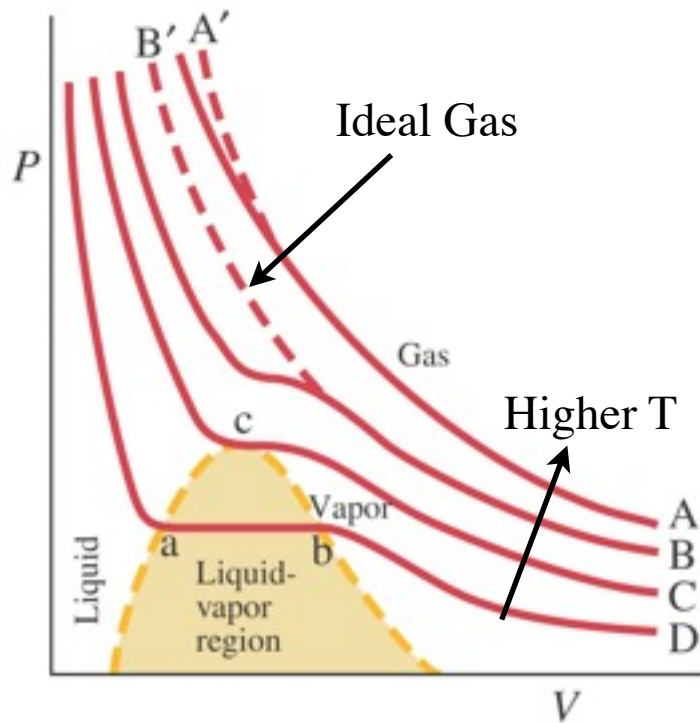


In curve D, the gas becomes **liquid**; it begins condensing at (b) and is entirely liquid at (a). The point (c) is called the **critical point**.

Below the **critical temperature** $T_C$, the gas can **liquefy** if the pressure is sufficient; above it, no amount of **pressure** will suffice.

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# 18-3 Real Gases and Changes of Phase

**A *PT* diagram is called a phase diagram; it shows all three phases of matter. The *PV* diagram below shows the liquid and vapor phases at different temperatures.**



H₂O Phase Diagram

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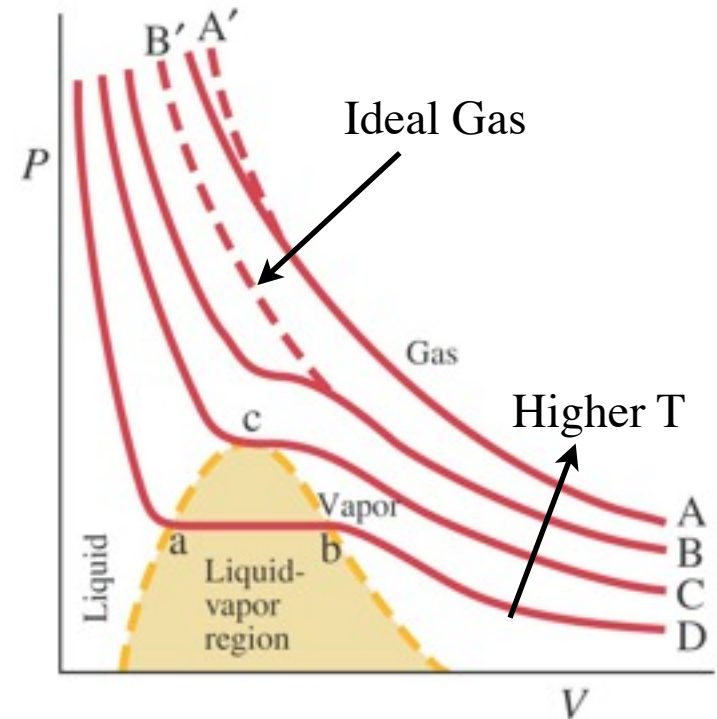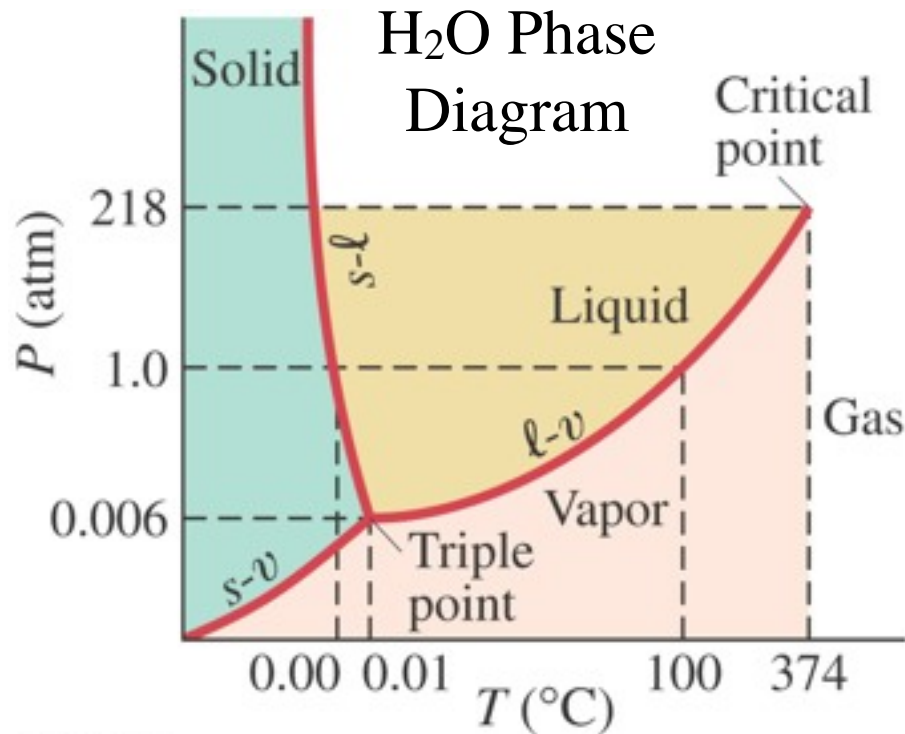
# 18-3 Real Gases and Changes of Phase

**Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.**

TABLE 18–1 Critical Temperatures and Pressures

| Substance | Critical Temperature °C | Critical Temperature K | Critical Pressure (atm) |
|---|---|---|---|
| Water | 374 | 647 | 218 |
| $CO_2$ | 31 | 304 | 72.8 |
| Oxygen | −118 | 155 | 50 |
| Nitrogen | −147 | 126 | 33.5 |
| Hydrogen | −239.9 | 33.3 | 12.8 |
| Helium | −267.9 | 5.3 | 2.3 |

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# 18-3 Real Gases and Changes of Phase

A $PT$ diagram is called a **phase diagram**; it shows all three phases of matter. The solid-liquid transition is **melting** or **freezing**; the liquid-vapor one is **boiling** or **condensing**; and the solid-vapor one is **sublimation**.



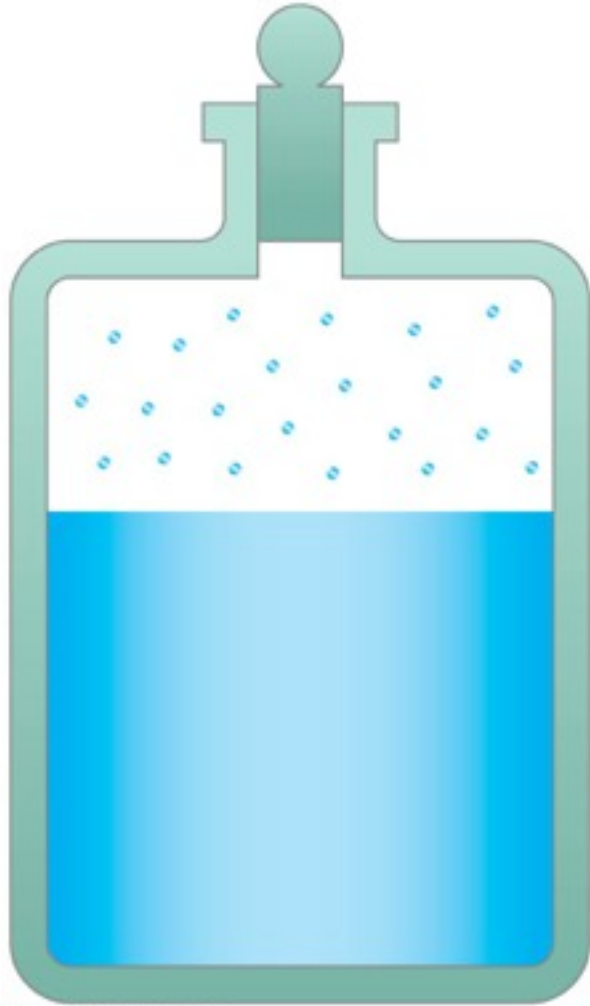H₂O Phase Diagram

CO₂ Phase Diagram

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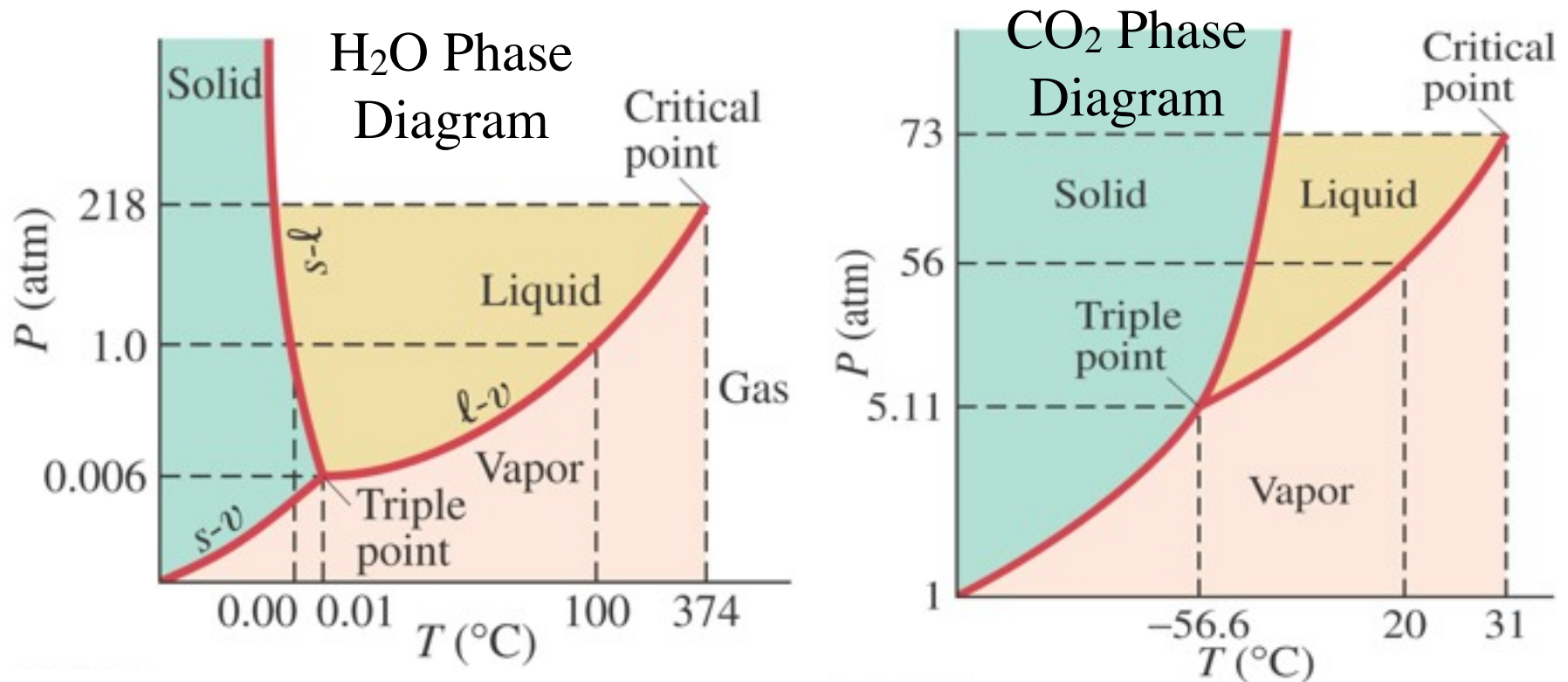
**The triple point is the only point where all three phases can coexist in equilibrium.**

**Below the critical temperature $T_C$, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.**



H$_2$O Phase Diagram

CO$_2$ Phase Diagram

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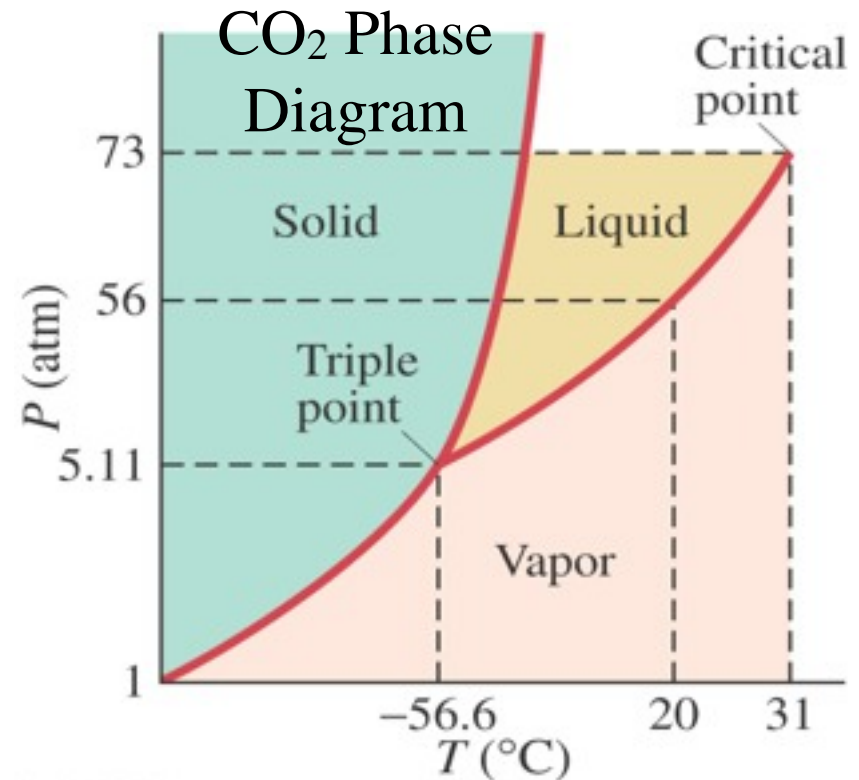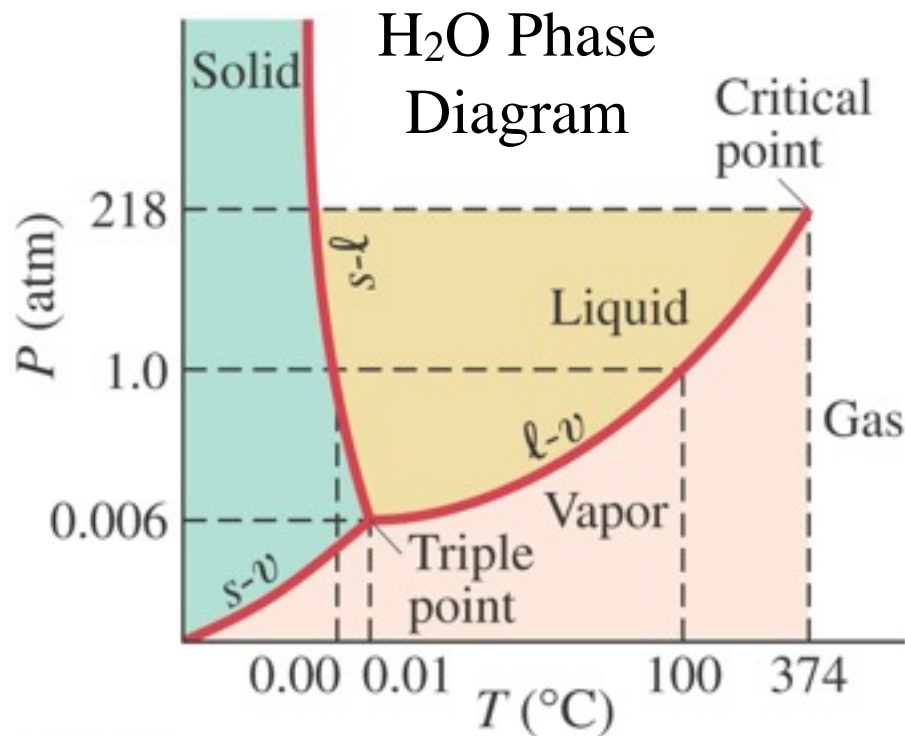
# 18-4 Vapor Pressure and Humidity

An open container of water can **evaporate**, rather than boil, away. The **fastest** molecules are escaping from the water's surface, so evaporation is a **cooling** process as well.

The inverse process is called **condensation**.

When the evaporation and condensation processes are in **equilibrium**, the vapor just above the liquid is said to be **saturated**, and its pressure is the **saturated vapor pressure**.

Monday, October 7, 13

# 18-4 Vapor Pressure and Humidity

**TABLE 18–2 Saturated Vapor Pressure of Water**

| Temp-erature (°C) | Saturated Vapor Pressure | |
|---|---|---|
| | torr (= mm-Hg) | Pa (= N/m²) |
| −50 | 0.030 | 4.0 |
| −10 | 1.95 | $2.60 \times 10^2$ |
| 0 | 4.58 | $6.11 \times 10^2$ |
| 5 | 6.54 | $8.72 \times 10^2$ |
| 10 | 9.21 | $1.23 \times 10^3$ |
| 15 | 12.8 | $1.71 \times 10^3$ |
| 20 | 17.5 | $2.33 \times 10^3$ |
| 25 | 23.8 | $3.17 \times 10^3$ |
| 30 | 31.8 | $4.24 \times 10^3$ |
| 40 | 55.3 | $7.37 \times 10^3$ |
| 50 | 92.5 | $1.23 \times 10^4$ |
| 60 | 149 | $1.99 \times 10^4$ |
| 70[†] | 234 | $3.12 \times 10^4$ |
| 80 | 355 | $4.73 \times 10^4$ |
| 90 | 526 | $7.01 \times 10^4$ |
| 100[‡] | 760 | $1.01 \times 10^5$ |
| 120 | 1489 | $1.99 \times 10^5$ |
| 150 | 3570 | $4.76 \times 10^5$ |

[†]Boiling point on summit of Mt. Everest.
[‡]Boiling point at sea level.

**The saturated vapor pressure increases with temperature.**

Boiling point on summit of Mt. Everest

Boiling point in airplane
Boiling point at sea level

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# 18-4 Vapor Pressure and Humidity



**A liquid boils when its saturated vapor pressure equals the external pressure.**

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# 18-4 Vapor Pressure and Humidity

**Partial** pressure is the pressure each component of a mixture of gases would exert if it were the only gas present. The partial pressure of water in the air can be as low as zero, and as high as the saturated vapor pressure at that temperature.

**Relative humidity** is a measure of the saturation of the air.

$$\text{Relative humidity} = \frac{\text{partial pressure of } H_2O}{\text{saturated vapor pressure of } H_2O} \times 100\%.$$

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# 18-4 Vapor Pressure and Humidity

**When the humidity is high, it feels muggy; it is hard for any more water to evaporate.**

**Neuschwanstein Castle
Bavaria, Germany**

**The dew point is the temperature at which the air would be saturated with water.**

**If the temperature goes below the dew point, dew, fog, or even rain may occur.**

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# 18-5 Van der Waals Equation of State

To get a more realistic model of a gas, we include the finite size of the molecules and the range of the intermolecular force beyond the size of the molecule.



$2r$

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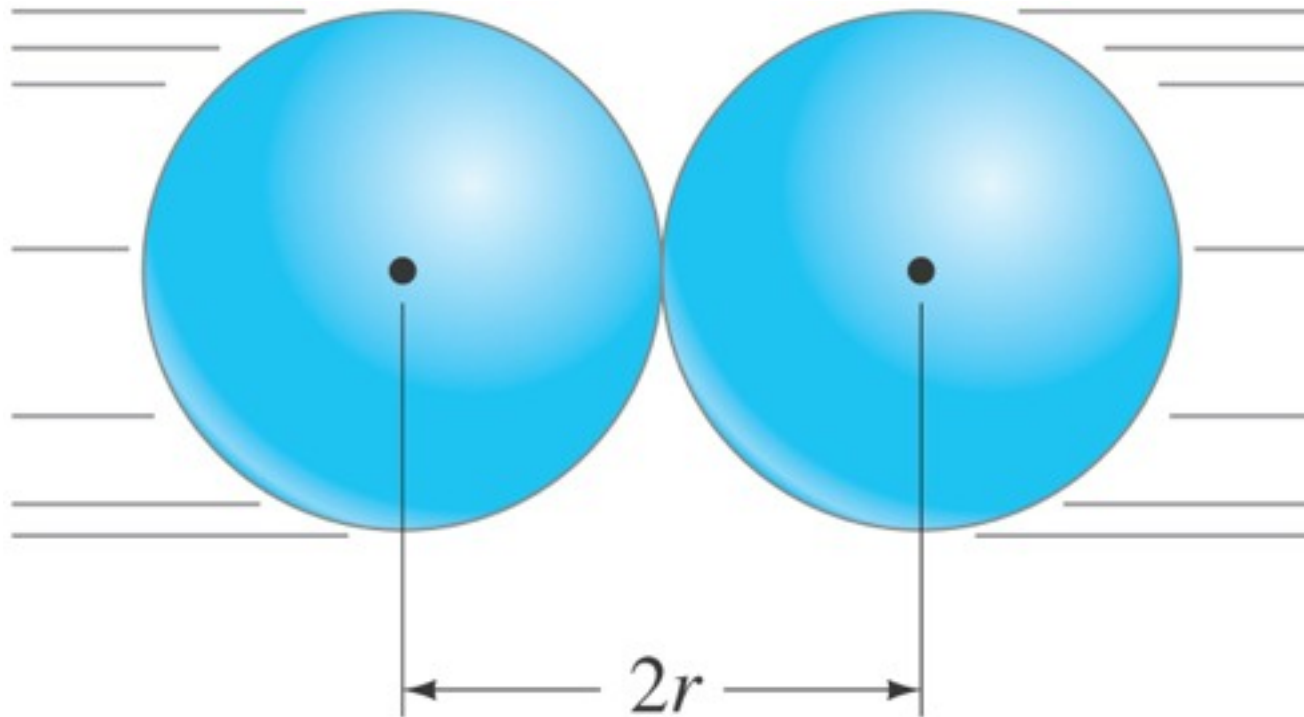
# 18-5 Van der Waals Equation of State

We assume that some fraction $b$ of the volume per mole is unavailable due to the finite size of the molecules. We also expect that the pressure will be reduced by a factor proportional to the square of the density, due to interactions between the molecules. This gives the Van der Waals equation of state; the constants $a$ and $b$ are found experimentally for each gas:

$$\left( P + \frac{a}{(V/n)^2} \right) \left( \frac{V}{n} - b \right) = RT.$$

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# 18-5 Van der Waals Equation of State

**The $PV$ diagram for a Van der Waals gas fits most experimental data quite well.**

$$\left(P + \frac{a}{(V/n)^2}\right)\left(\frac{V}{n} - b\right) = RT.$$
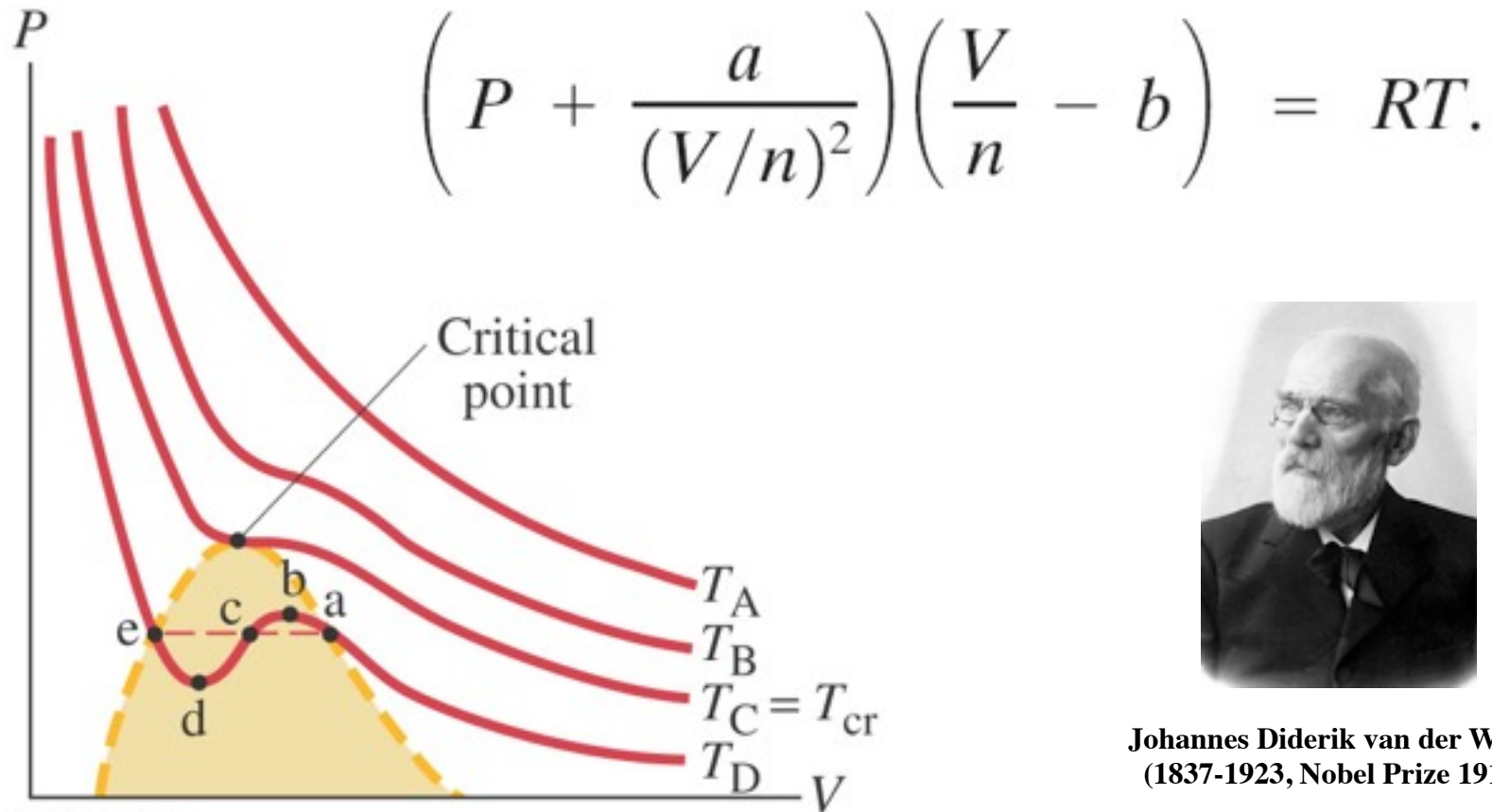


Johannes Diderik van der Waals
(1837-1923, Nobel Prize 1910)

Monday, October 7, 13