PHYS 1P22/92

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13. Temperature, Kinetic Theory, and the Gas Laws
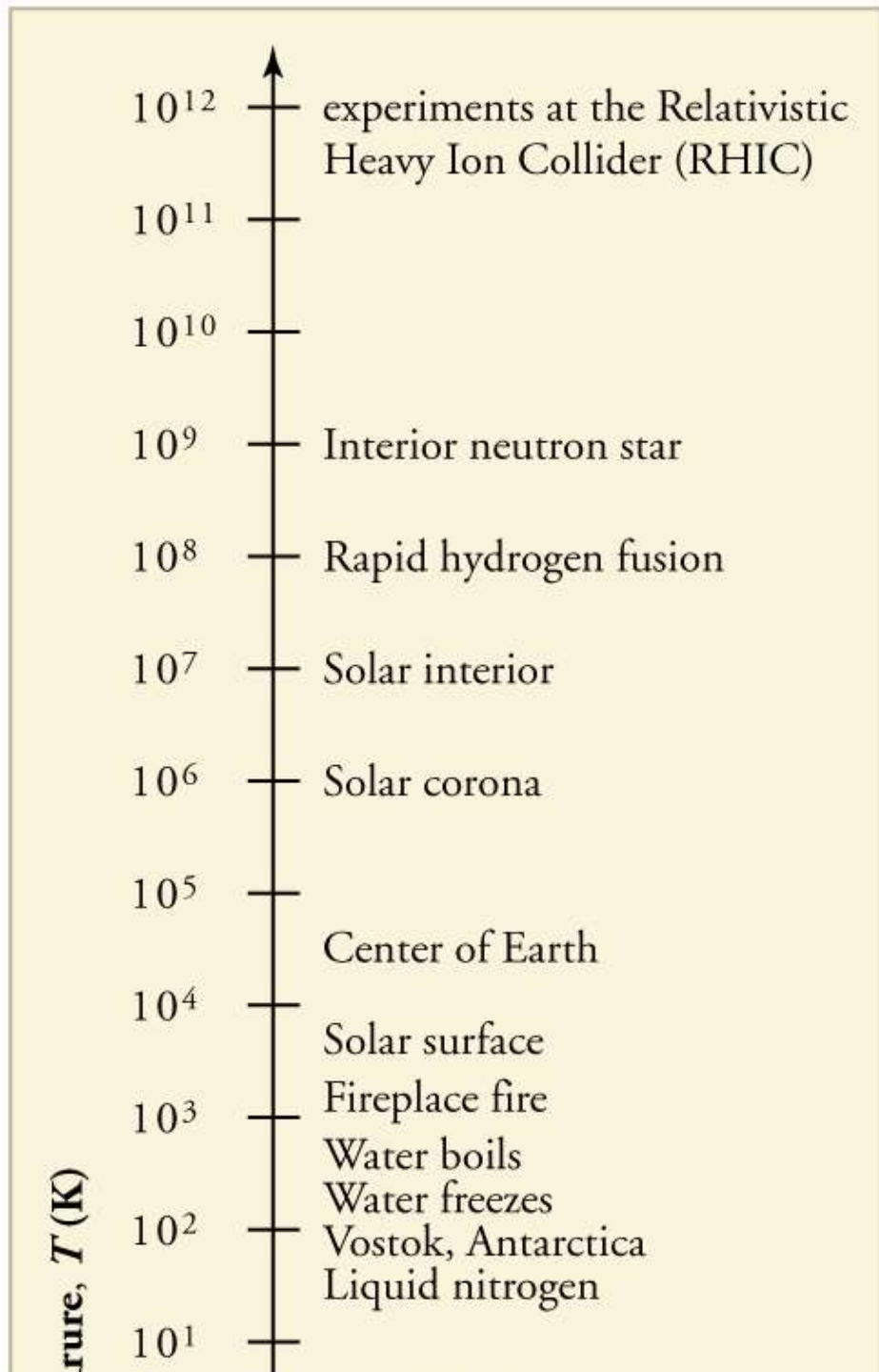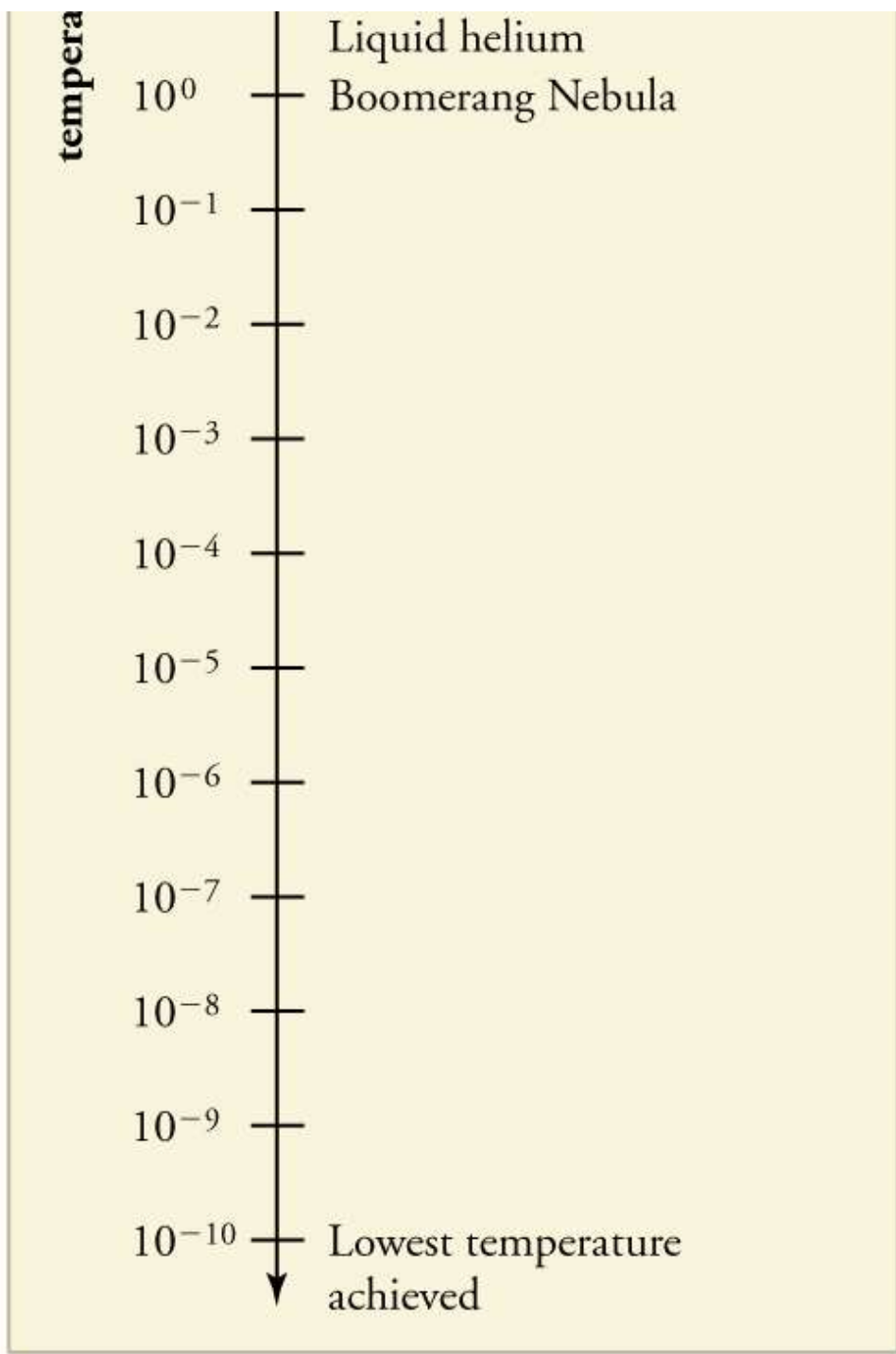
13.1 Temperature

Temperature scales and units

- **The Celsius scale:** Defined by setting the freezing point of water at 0 °C and boiling point at 100 °C, at 1 atm (atmospheric pressure).

- **The Kelvin scale:** Starts from $0 \text{ K} \equiv -273.15$ °C, absolute zero, the coldest possible temperature.
  - Celsius is defined in terms of kelvin. Precise definition, not approximation.

- Notation:
  - Just K, no ° symbol.
  - Just "kelvin" or "kelvins", not "degrees kelvin".
  - Unit name (kelvin) not capitalized. (Like newton, pascal, etc.)

Temperature scales and units

- Kelvin is always positive; nothing can be colder than 0 K, or even exactly 0 K. Celsius can be positive or negative, down to 0 K $\equiv$ $-273.15\,°C$.

- To convert: kelvin = Celsius + 273.15, Celsius = kelvin − 273.15.

- Example: "Room temperature" usually means 25 °C. This is $273.15 + 25 = 298.15$ K.

- The Fahrenheit scale: Used only in the US and Liberia. Useless for doing science. We won't use it in this course.

Temperature examples (logarithmic scale)

temperature

10^0	Liquid helium
	Boomerang Nebula
10^{-1}	
10^{-2}	
10^{-3}	
10^{-4}	
10^{-5}	
10^{-6}	
10^{-7}	
10^{-8}	
10^{-9}	
10^{-10}	Lowest temperature achieved

temperature, T (K)

10^{12}	experiments at the Relativistic Heavy Ion Collider (RHIC)
10^{11}	
10^{10}	
10^9	Interior neutron star
10^8	Rapid hydrogen fusion
10^7	Solar interior
10^6	Solar corona
10^5	
	Center of Earth
10^4	
	Solar surface
10^3	Fireplace fire
	Water boils
	Water freezes
10^2	Vostok, Antarctica
	Liquid nitrogen
10^1	

Thermal equilibrium

- Two systems are in thermal contact if heat can transfer between them.

- Any two systems in thermal contact and isolated from the environment will reach the same temperature.

- We say they reached thermal equilibrium, and no further heat flow or temperature changes will occur.

- That's how a thermometer works: it reaches thermal equilibrium with an object and then measures its own temperature.

- A single object is in internal thermal equilibrium if no heat is flowing within it – its temperature is uniform.

Zeroth law of thermodynamics

- The zeroth law of thermodynamics: If systems A and B are in thermal equilibrium, and B is in thermal equilibrium with system C, then A is also in thermal equilibrium with C.
    - In other words: Thermal equilibrium is transitive.
    - This law may seem obvious, but it is required to justify the use of thermometers: If two thermometers touch the same object, then they must read the same temperature.
    - We will learn more laws of thermodynamics in chapter 15.

When to use Celsius vs. kelvin

- Given two temperatures T_1 and T_2 expressed in Celsius, the difference is
$$\Delta T = T_2 - T_1$$

- But if we convert to kelvins first, the 273.15 cancels and we get
$$(T_2 + 273.15) - (T_1 + 273.15) = T_2 - T_1 = \Delta T$$

- So for a **temperature difference** ΔT, either Celsius or kelvins can be used.

- However, temperature difference is the **only** time degrees Celsius are valid. In all other cases, kelvins must be used.

- If unsure, use kelvins, because they can be used in any situation, both for temperature difference and for absolute temperature.

13.2 Thermal Expansion of Solids and Liquids

- Materials generally expand when heated and contract when cooled.

- A thermometer works by measuring how much a substance (e.g. mercury or alcohol) expands.
  - The container (glass, plastic) also expands, but much less.

- Hot air rises because it expands, so its density decreases compared to the surrounding air.

- Structures such as railroad tracks and bridges must have expansion joints to allow for expansion and contraction.
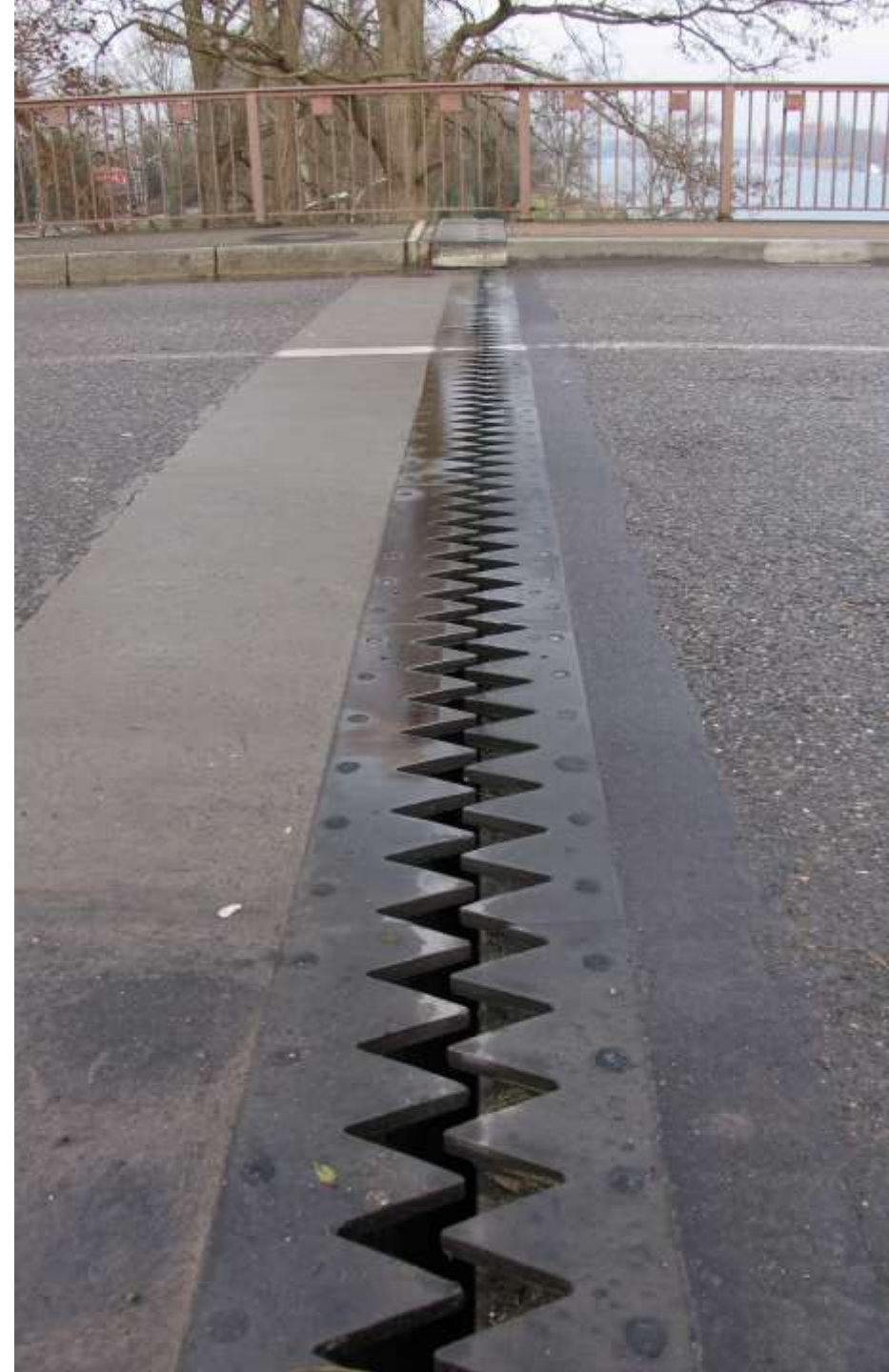
Linear (1D) thermal expansion

- The change in length ΔL of a material is

$$\Delta L = \alpha L \Delta T$$

  - L is the original length.
  - ΔT is the change in temperature.
  - α is the coefficient of linear expansion for the specific material at the appropriate temperature. Measured in K^{-1} (inverse kelvin) or equivalently $(°C)^{-1}$.

- This equation only works if:
  - ΔT is small enough that α doesn't change much (since it depends on T).
  - The fractional change in length $\Delta L / L$ is small.

- If these conditions do not hold, we must use calculus.

Area (2D) thermal expansion

- The change in area ΔA of a material is
$$\Delta A = 2\alpha A \Delta T$$

  - A is the original area.

  - ΔT is the change in temperature.

  - α is the coefficient of linear expansion.

- As in 1D, this equation only works if ΔT and $\Delta A / A$ are small.

Volume (3D) thermal expansion

- The change in volume ΔV of a material is
$$\Delta V = \beta V \Delta T$$

  - V is the original area.

  - ΔT is the change in temperature.

  - β is the coefficient of volume expansion. Usually $\beta \approx 3\alpha$.

- This equation only works if ΔT and $\Delta V / V$ are small.

- Some examples of how rigid objects expand (solid: original, dashed: after expansion):
  - Left: The area increases due to expansion in both directions.
  - Center: The hole in the center expands as if it was filled.
  - Right: The volume increases due to expansion in all 3 directions.
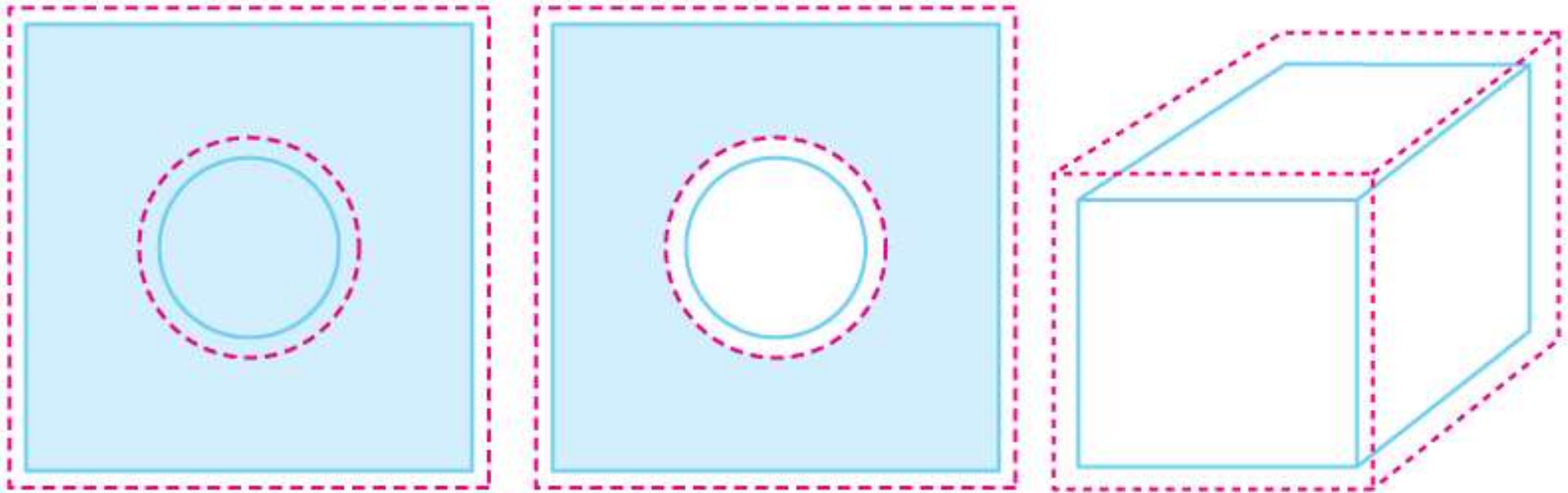
Approximate thermal expansion coefficients of solids at 20 °C

Material	α ($\times 10^{-6}$ K^{-1})	β ($\times 10^{-6}$ K^{-1})
Aluminum	25	75
Brass	19	56
Copper	17	51
Gold	14	42
Iron or Steel	12	35
Invar (Nickel-iron alloy)	0.9	2.7
Lead	29	87
Silver	18	54
Glass (ordinary)	9	27
Glass (Pyrex)	3	9
Quartz	0.4	1
Concrete, Brick	12	36
Marble (average)	7	21

Approximate volumetric thermal expansion coefficients of liquids at 20 °C

Material	β ($\times$ 10^{-6} K^{-1})
Ether	1650
Ethyl alcohol	1100
Petrol	950
Glycerin	500
Mercury	180
Water	210

For air and most other gases at atmospheric pressure:
$\beta \approx 3400 \times 10^{-6}$ K^{-1}

- **Class problem:** The main span of San Francisco's Golden Gate Bridge is 1275 m long at its coldest. The bridge is exposed to temperatures ranging from – 15 °C to 40 °C. What is its change in length between these temperatures? Assume that the bridge is made entirely of steel ($\alpha \approx 12 \times 10^{-6}$ K).

- **Solution:**

$$\Delta L = \alpha L \Delta T \approx (12 \times 10^{-6} \text{ K}^{-1})(1275 \text{ m})\left(\left(40 - (-15)\right) \text{K}\right)$$
$$= 12 \times 10^{-6} \cdot 1275 \cdot \left(40 - (-15)\right) \text{K}^{-1} \cdot \text{m} \cdot \text{K}$$
$$\approx 0.84 \text{ m}$$

- This is a significant change; it is spread over many expansion joints.

- Water is an important exception. Above 4 °C it expands as temperature increases, but between 0 °C and 4 °C it **contracts** as temperature increases.

- Pop Quiz: How can the surface of a pond freeze while the water below stays liquid at 4 °C?

- Answer: Because liquid at 4 °C has a larger density than ice at 0 °C, so it sinks.

Density of Freshwater

Density (g/cm^3) vs. Temperature (°C)
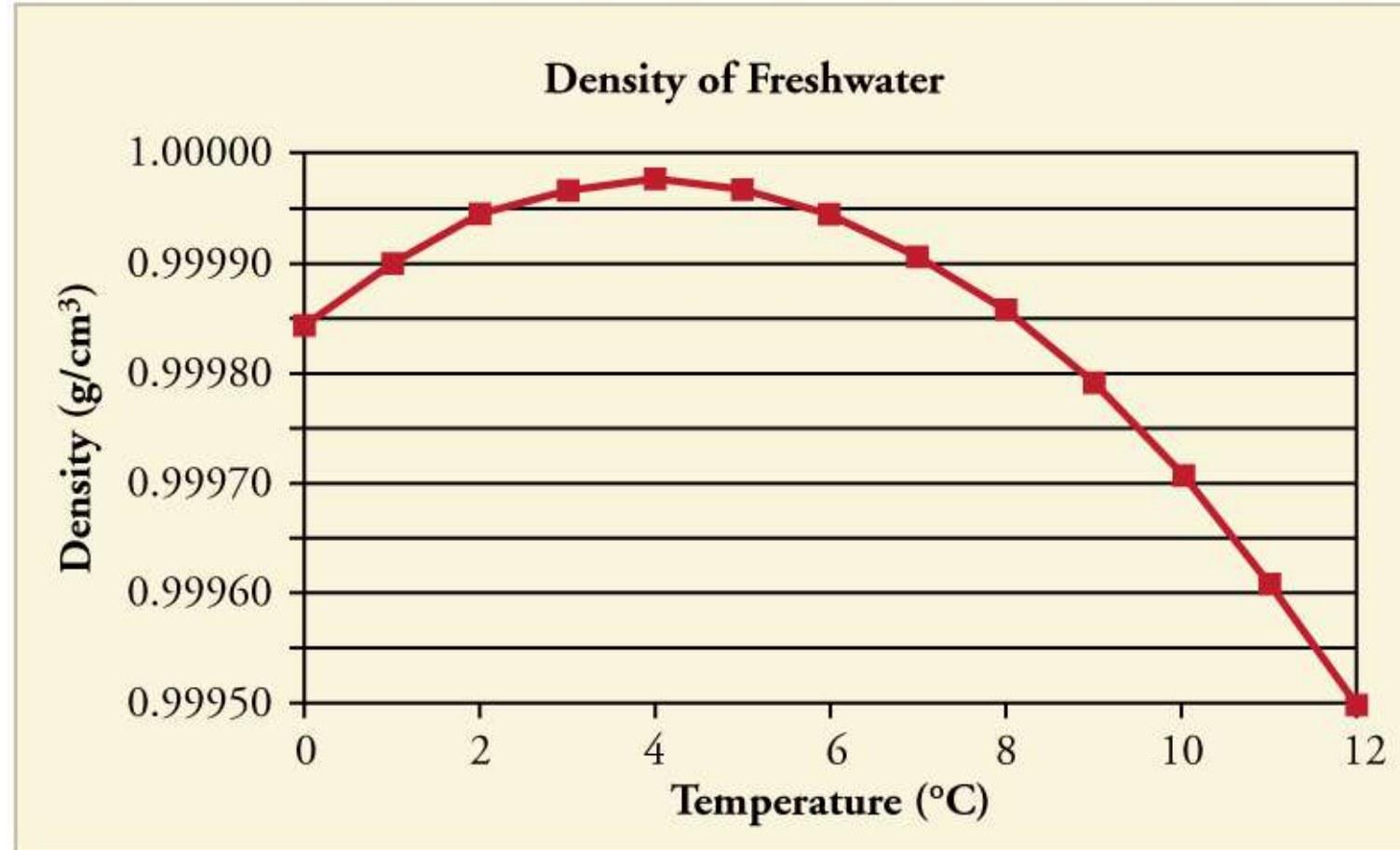
- **Class problem:** A steel gasoline tank of volume V is full of gas. Both the tank and the gasoline have a temperature of T_1. How much gasoline has spilled by the time they warm to T_2?

- **Solution:** Both the gasoline and the tank itself expand from volume V:

$$\Delta V_s = \beta_s V \Delta T, \qquad \Delta V_g = \beta_g V \Delta T$$

The gasoline is spilled because it expanded more than the steel. The total amount spilled is:

$$
\begin{aligned}
V_{\text{spilled}} &= \Delta V_g - \Delta V_s \\
&= \beta_g V \Delta T - \beta_s V \Delta T \\
&= (\beta_g - \beta_s) V \Delta T
\end{aligned}
$$

- **Problem:** Calculate V_{spilled} if $V \approx 60.0$ L, $T_1 \approx 15.0\ °C$, $T_2 \approx 35.0\ °C$, $\beta_s \approx 35.0 \times 10^{-6}\ K^{-1}$, $\beta_g \approx 950 \times 10^{-6}\ K^{-1}$. Do a sanity check on units and numerical value.

- **Solution:**

$$
\begin{aligned}
V_{\text{spilled}} &= \left(\beta_g - \beta_s\right) V \Delta T \\
&\approx (950 - 35) \times 10^{-6}\ K^{-1} \cdot 60 \times 10^{-3}\ m^3 \cdot (35 - 15)\ K \\
&= 915 \times 10^{-6} \cdot 60 \times 10^{-3} \cdot 20\ m^3 \\
&\approx 1.10 \times 10^{-3}\ m^3
\end{aligned}
$$

- Sanity check:
  - Units are correct for volume.
  - Amount spilled is around 1 L, which is less than the total of 60 L. It seems a bit too large, but the gasoline does expand $915/35 \approx 26$ times faster than the steel.

- If the tank is sealed, it will burst (both liquids and solids are incompressible). Tanks usually have air gaps to prevent this.

13.3 The Ideal Gas Law

Ideal gas

- Particles (atoms and/or molecules) in a gas are very far apart and interact only weakly.

- In an ideal gas, the particles do not interact at all (but they can collide elastically).

- Many real gasses behave like ideal gases under certain conditions, for example air at room temperature.

The ideal gas law

- An ideal gas satisfies an equation of state called the ideal gas law:

$$PV = Nk_BT$$

  - P is the **absolute** pressure ($0 = $ no pressure; **do not** use gauge pressure!)
  - V is the volume.
  - N is the number of particles.
  - T is the **absolute** temperature ($0 = $ absolute zero; **do not** use Celsius!).
  - $k_B \equiv 1.380649 \times 10^{-23}$ J/K is the Boltzmann constant (exact definition).
    - In terms of SI base units: $\frac{J}{K} = \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2\cdot\text{K}} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1}$

- **Problem:** A bicycle tire is fully inflated, with absolute pressure P_1 at temperature T_1. What is the pressure P_2 after its temperature has risen to $T_2 > T_1$? Assume that there are no appreciable leaks or changes in volume.

- **Solution:** N is constant (no leaks) and V is constant. Initially we have
$$P_1 V = N k_B T_1$$

In the end we have
$$P_2 V = N k_B T_2$$

Divide the two equations and solve for P_2:
$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \Longrightarrow \quad P_2 = P_1 \frac{T_2}{T_1}$$

- **Problem:** Calculate P_2 if $P_1 = 7.00 \times 10^5$ Pa, $T_1 = 18.0\,°\text{C}$, $T_2 = 35.0\,°\text{C}$.

- **Solution:** We must convert the temperatures to kelvins. The ideal gas law only makes sense with an **absolute** temperature scale, which starts from 0 at absolute zero. Recall that

$$\text{kelvin} = \text{Celsius} + 273.15$$

So we get:

$$P_2 = P_1 \frac{T_2}{T_1}$$

$$\approx (7.00 \times 10^5 \text{ Pa}) \frac{(35.0 + 273.15) \text{ K}}{(18.0 + 273.15) \text{ K}}$$

$$\approx 7.41 \times 10^5 \text{ Pa}$$

- Class problem: Use the ideal gas law $PV = Nk_BT$ to calculate the number of molecules in 1.0000 m^3 of air at temperature 0 °C and atmospheric pressure $P_{atm} \equiv 101{,}325$ Pa.
  - Recall that $k_B \equiv 1.380649 \times 10^{-23}$ J/K and kelvin = Celsius + 273.15.

- Solution:

$$N = \frac{PV}{k_BT} = \frac{(101{,}325 \text{ Pa})(1 \text{ m}^3)}{(1.380649 \times 10^{-23} \text{ J/K})(273.15 \text{ K})}$$

$$= \frac{101{,}325}{1.380649 \times 10^{-23} \cdot 273.15} \frac{\text{Pa} \cdot \text{m}^3}{\text{J}}$$

$$\approx 2.6868 \times 10^{25}$$

Unit calculation: $\text{Pa} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$ and $\text{J} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$, so:

$$\frac{\text{Pa} \cdot \text{m}^3}{\text{J}} = \frac{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \cdot \text{m}^3}{\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}} = 1 \text{ (pure number)}$$

Moles and Avogadro's constant

- A mole (or mol) is the amount of a substance that contains as many particles as there are atoms in 12 grams of carbon-12.

- The number of particles in a mole is Avogadro's constant N_A:
$$N_A \equiv 6.02214076 \times 10^{23} \text{ mol}^{-1} \quad \text{(Note: exact definition)}$$

- Avogadro's number (sometimes denoted N_0) is the numerical value of Avogadro's constant (i.e. without the units of inverse moles). So $N_A \equiv N_0 \text{ mol}^{-1}$.

  Note: Moles and Avogadro's constant are not really necessary to do science. They are used to count things, but we could just express the number of particles as a pure number without units, and it would be much less confusing. However, they are used for historical reasons.

Molar mass

- The molar mass of a substance is the ratio between its mass (in grams) and the amount of substance (in moles). Units: g/mol.
  - In other words, a mole of a substance has a mass in grams equal to its molar mass.
  - Molar mass is the same as atomic mass (the mass of a single atom) but expressed in g/mol…
  - The atomic masses of elements are given in the periodic table, and in Appendix A of the textbook.
- Example: The molar mass of carbon-12 is 12 g/mol.

The ideal gas law in terms of moles

- If a substance contains N particles, then it has $n \equiv N/N_A$ moles.

- Since $N = nN_A$, we can rewrite the ideal gas law:
$$PV = Nk_BT = nN_Ak_BT$$

- If we define the universal gas constant $R \equiv N_Ak_B$, we obtain the ideal gas law in terms of moles:
$$PV = nRT$$

- We won't use this, or moles and Avogadro's constant in general, in our course. But you might see it elsewhere.

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

- Consider a gas in a cubic box of size L.

- The gas particles collide with the walls of the box in the x direction with speed v_x.

- We assume for simplicity that the speed is $-v_x$ after the collision.

- The change in speed is $\Delta v_x = v_x - (-v_x) = 2v_x$, so the change in momentum is $\Delta p = m\Delta v_x = 2mv_x$. The force is

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\Delta t}$$

- Between collisions, the particle will bounce across the box and back. That's a distance $2L$ at speed v_x, so

$$\Delta t = \frac{2L}{v_x}$$
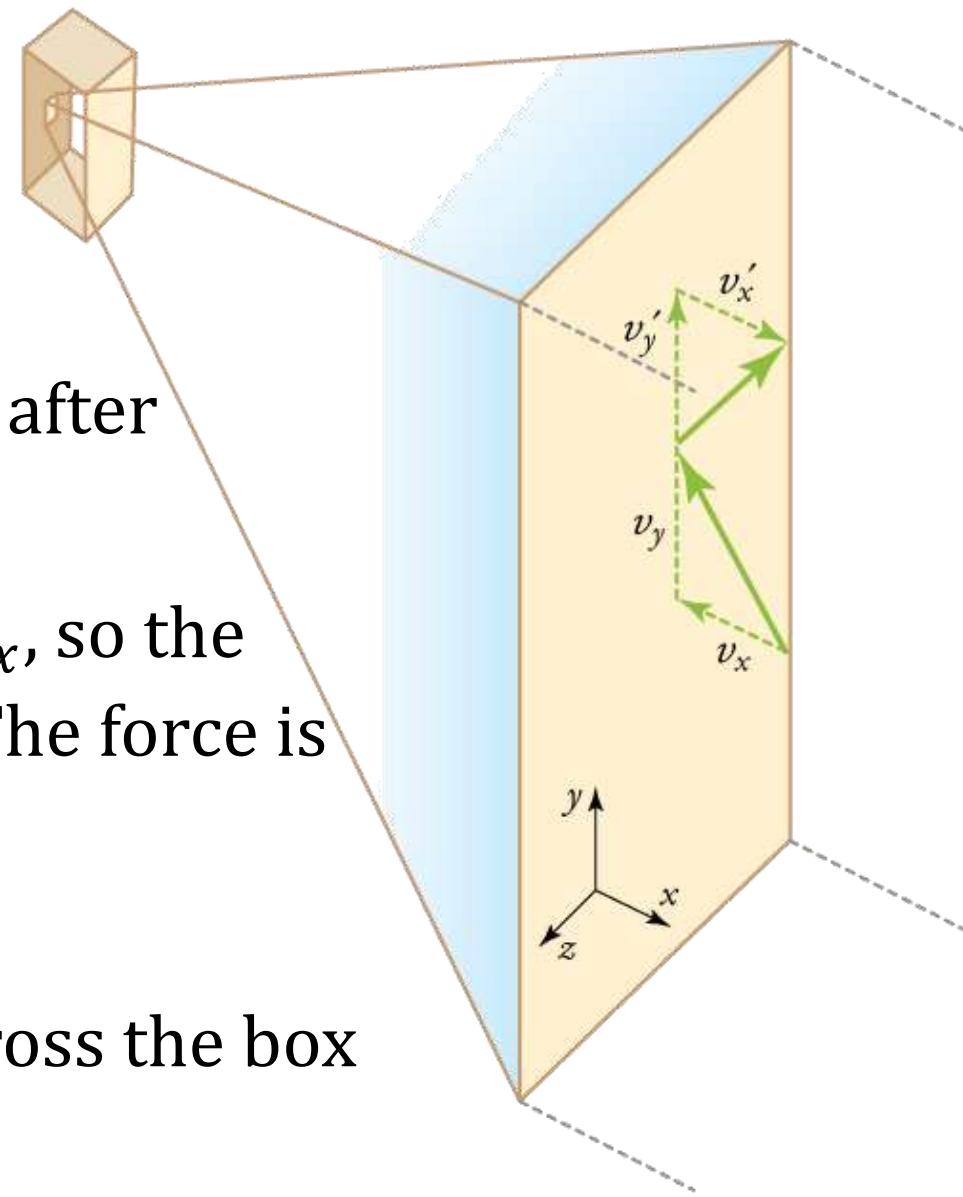
- We plug $\Delta t = 2L/v_x$ into the force:

$$F = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \implies LF = mv_x^2$$

- Now consider N particles moving in random directions. The average speed in all directions is identical (from symmetry, no direction is "special"):

$$v = v_x = v_y = v_z$$

- Summing vector components for the velocity, we have

$$|\mathbf{v}|^2 = v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2 \implies v_x^2 = \frac{v^2}{3}$$

- The pressure exerted by collisions from all N particles is ($A = L^2, V = L^3$):

$$P = \frac{NF}{A} = \frac{NF}{L^2} \implies PV = NLF = Nmv_x^2 = \frac{1}{3}Nmv^2$$

- The kinetic energy of the particle is

$$E_k = \frac{1}{2}mv^2 \implies mv^2 = 2E_k$$

- So we get

$$PV = \frac{1}{3}Nmv^2 = \frac{2}{3}NE_k$$

- On the other hand, from the ideal gas law $PV = Nk_BT$:

$$Nk_BT = \frac{2}{3}NE_k \implies E_k = \frac{1}{2}mv^2 = \frac{3}{2}k_BT$$

- We get a microscopic definition of temperature: it is proportional to the average (translational) kinetic energy of the particles.

$$T = \frac{2}{3k_B}E_k$$

- Equivalently, temperature is related to the average speed of the particles:

$$T = \frac{mv^2}{3k_B} \implies v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

- v_{rms} is the root-mean-square speed: the square root of the mean (average) square speed of all the particles.

- In a hotter gas, each particle will have more kinetic energy and will move at faster average speed.

- Class problem: What is the average kinetic energy of a gas molecule at 20.0 °C?
  - Use $k_B \equiv 1.380649 \times 10^{-23}$ J/K and kelvin = Celsius + 273.15.

- Solution:

$$E_k = \frac{3}{2} k_B T \approx \frac{3}{2} (1.380649 \times 10^{-23} \text{ J/K})(20 + 273.15) \text{ K} \approx 6.07 \times 10^{-21} \text{ J}$$

- Class problem: If the gas is composed of nitrogen molecules (N_2), what is the rms speed of a gas molecule at 20.0 °C?
  - Use $k_B \equiv 1.380649 \times 10^{-23}$ J/K and kelvin = Celsius + 273.15.
  - The mass of a nitrogen atom (N) is 2.3259×10^{-26} kg.

- Solution: (mass of N_2 is $2m$)

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{2m}} \approx \sqrt{\frac{3(1.380649 \times 10^{-23}\ \text{J/K})(20 + 273.15)\ \text{K}}{2(2.3259 \times 10^{-26}\ \text{kg})}}$$

$$= \sqrt{\frac{3(1.380649 \times 10^{-23})(20 + 273.15)}{2(2.3259 \times 10^{-26})}} \sqrt{\frac{\text{J}}{\text{kg}}}$$

$$\approx 511\ \text{m/s}$$

Unit conversion: $\text{J} = \text{kg} \cdot \text{m}^2/\text{s}^2$, so $\sqrt{\text{J/kg}} = \text{m/s}$.

- The probability distribution of speeds for particles a gas is given by the Maxwell-Boltzmann distribution.

- Note that the most probable speed v_p is less than v_{rms}.

- As temperature increases, the speeds are shifted to higher values and the distribution is broadened.
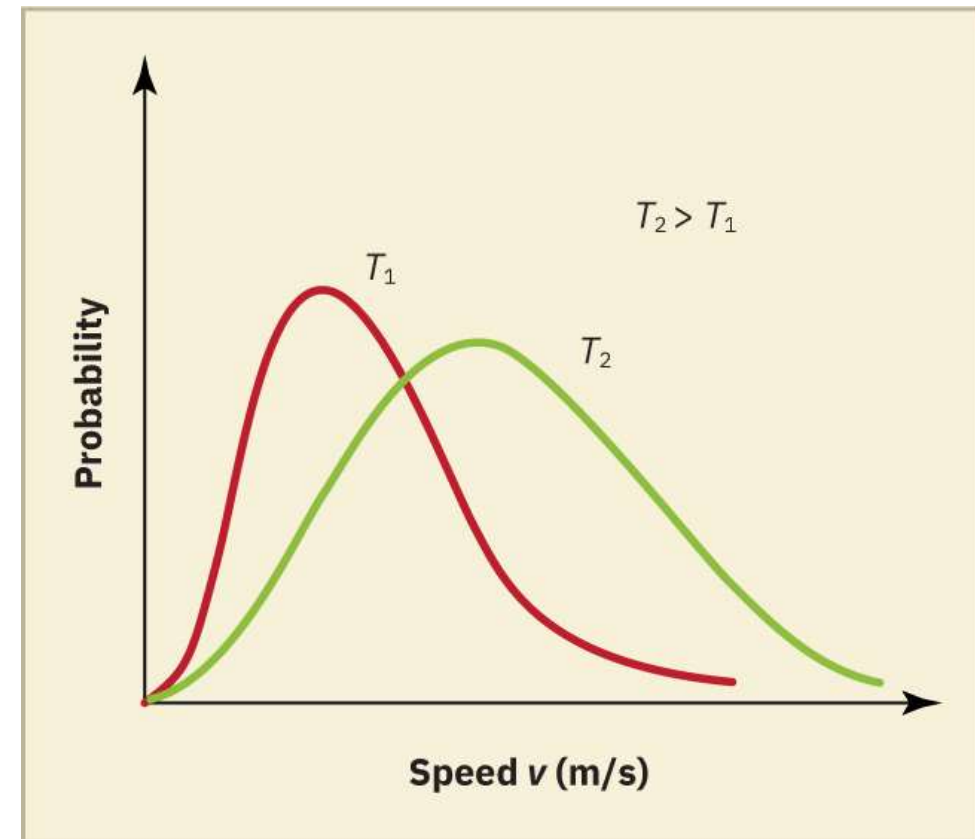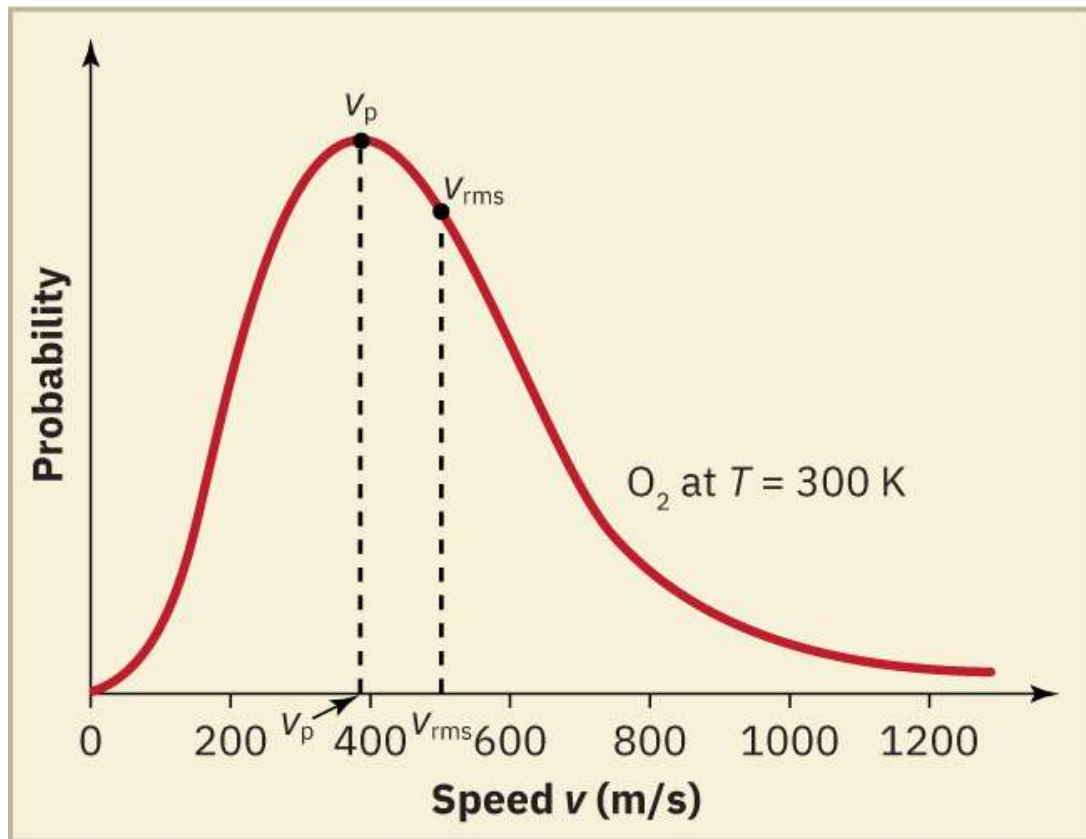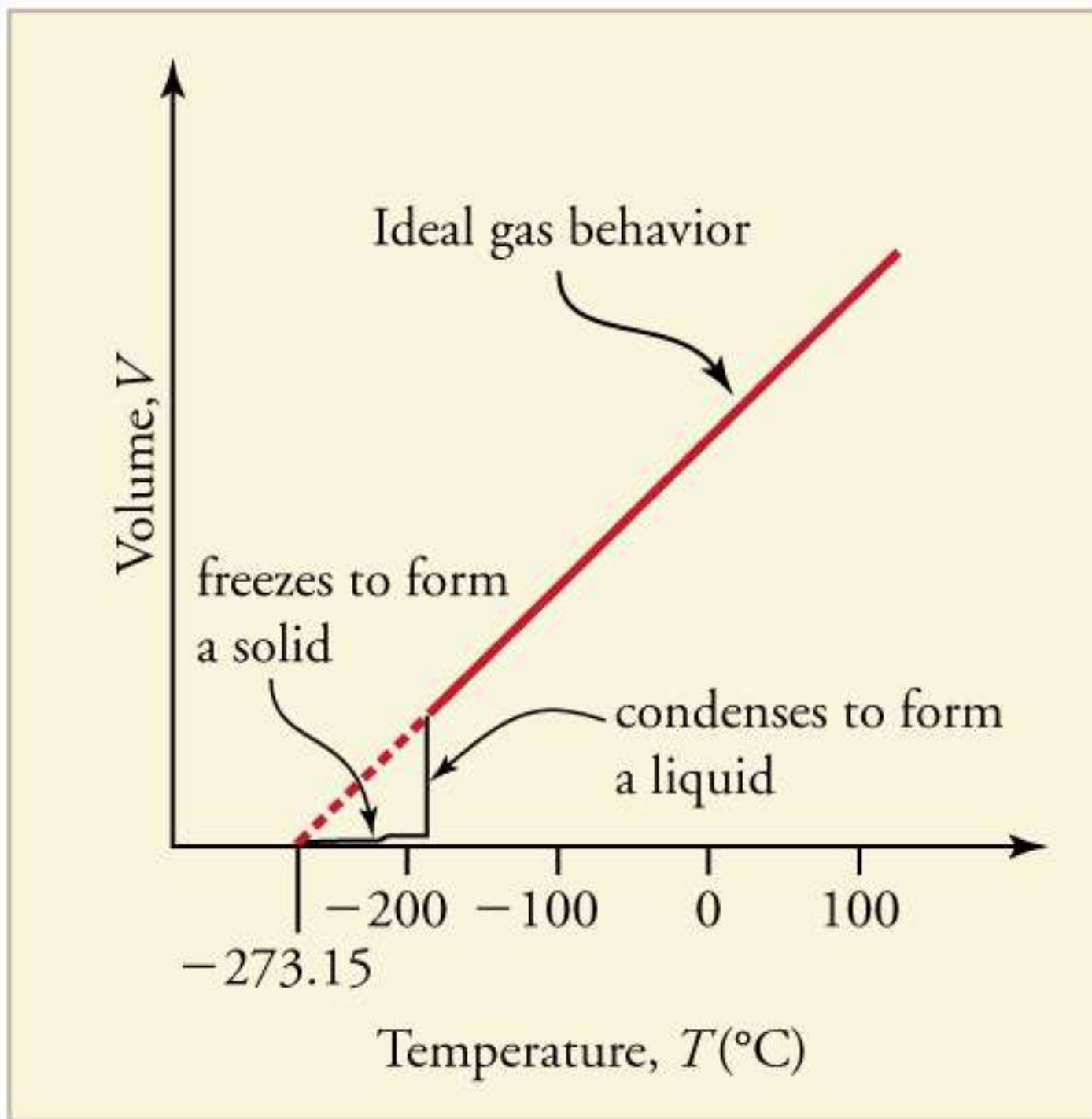
Simulation

- Simulation for an ideal gas:

  https://phet.colorado.edu/sims/html/gas-properties/latest/gas-properties_all.html

13.5 Phase Changes

- As a gas is cooled, it condenses to a liquid.

- There is a sudden drop in volume.

- Cooled even more, it freezes to a solid.

- The volume keeps decreasing, but doesn't reach zero because the molecules have a non-zero size.

- Recall the ideal gas law:
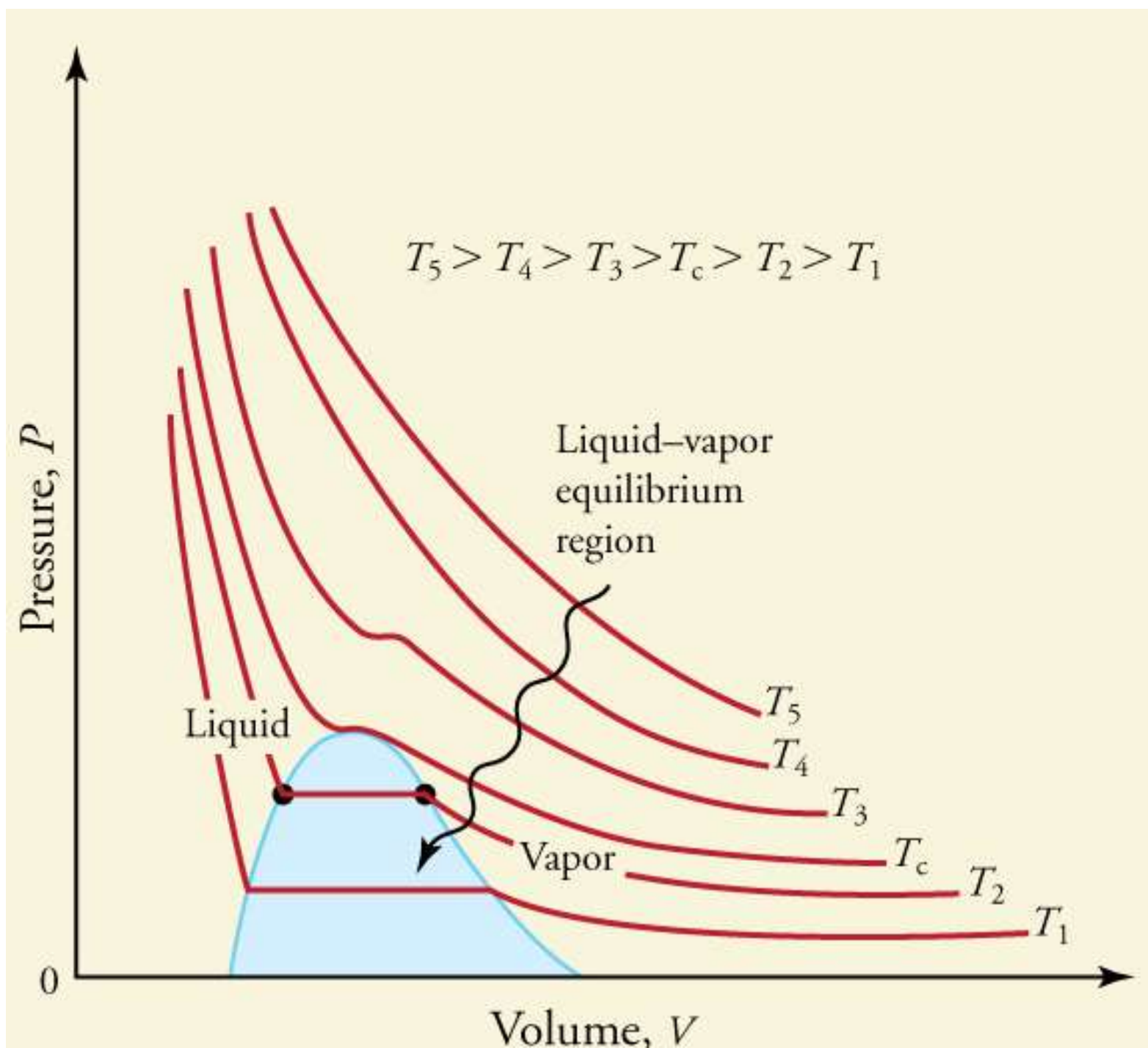$$PV = Nk_BT$$

- If N and T are fixed, then PV is constant.
  - So if P increases, V decreases, and vice versa.
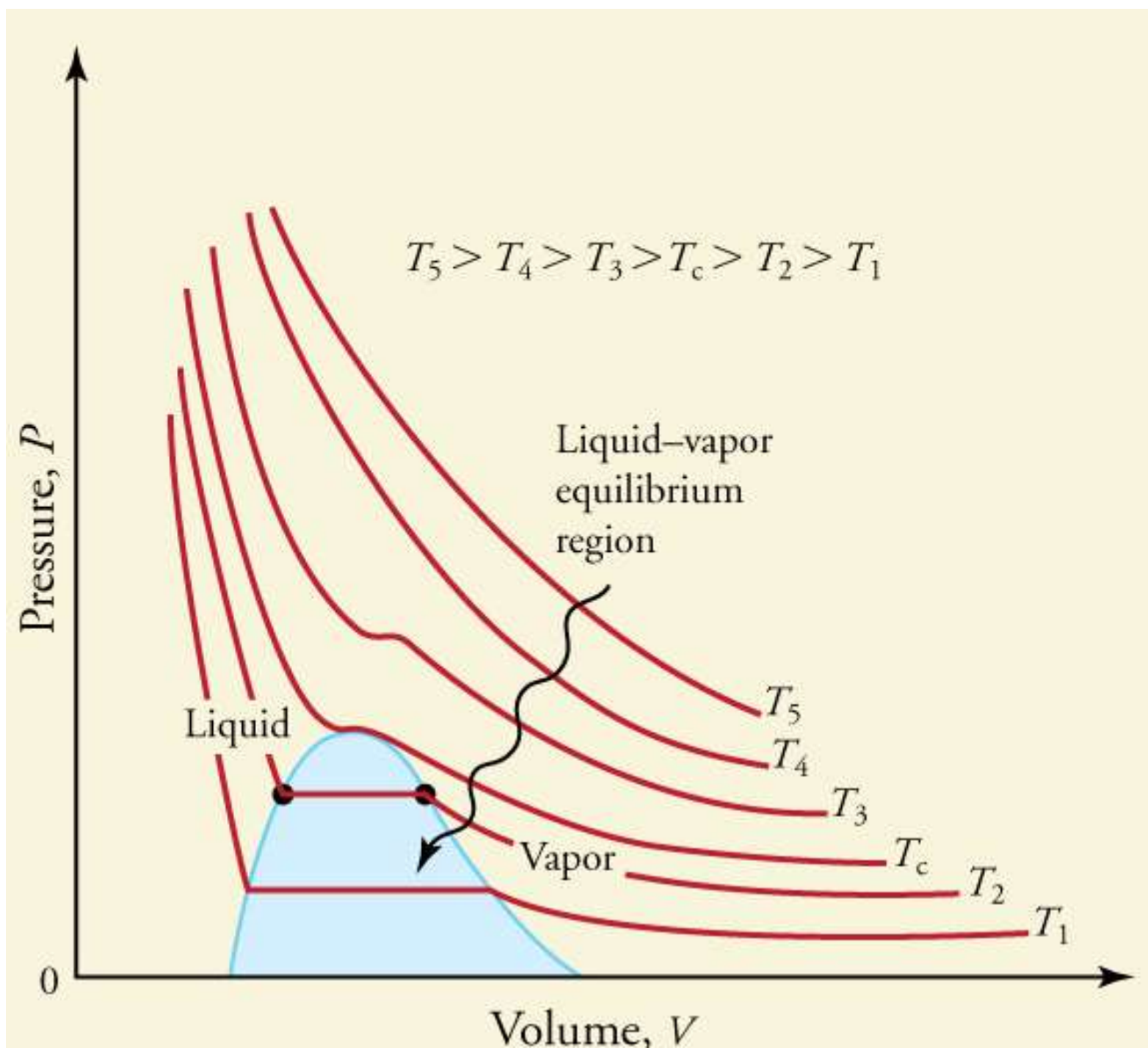
- Calling the constant $c \equiv Nk_BT$, we can write
$$PV = c \implies P = \frac{c}{V}$$

- The function has the shape of a hyperbola.

- Plotting this function for different values of c gives a PV diagram.

$T_5 > T_4 > T_3 > T_c > T_2 > T_1$

Liquid–vapor equilibrium region

Liquid

Vapor

T_5
T_4
T_3
T_c
T_2
T_1

Pressure, P

0

Volume, V

- $c \equiv N k_B T$ depends on temperature.

- So there is a different hyperbola for each T.

- Such a hyperbola is called an isotherm.

- At lower temperatures, the graphs look less like hyperbolas.

- The gas is not an ideal gas anymore, so $PV = c$ doesn't apply.

- It can even be a liquid at this point.

$T_5 > T_4 > T_3 > T_c > T_2 > T_1$

Liquid–vapor equilibrium region

Liquid

Vapor

T_5
T_4
T_3
T_c
T_2
T_1

Pressure, P

Volume, V

0

- There is a critical point or critical temperature T_c above which liquid cannot exist.

- At high pressure above the critical point, the gas will have the density of a liquid but will not condense.

  - E.g.: CO_2 cannot be liquefied above $\approx 31.0\ °C$.

- Critical pressure is the minimum pressure needed for liquid to exist at the critical temperature.

- Vapor is the gas phase when it exists at a temperature below the critical temperature.
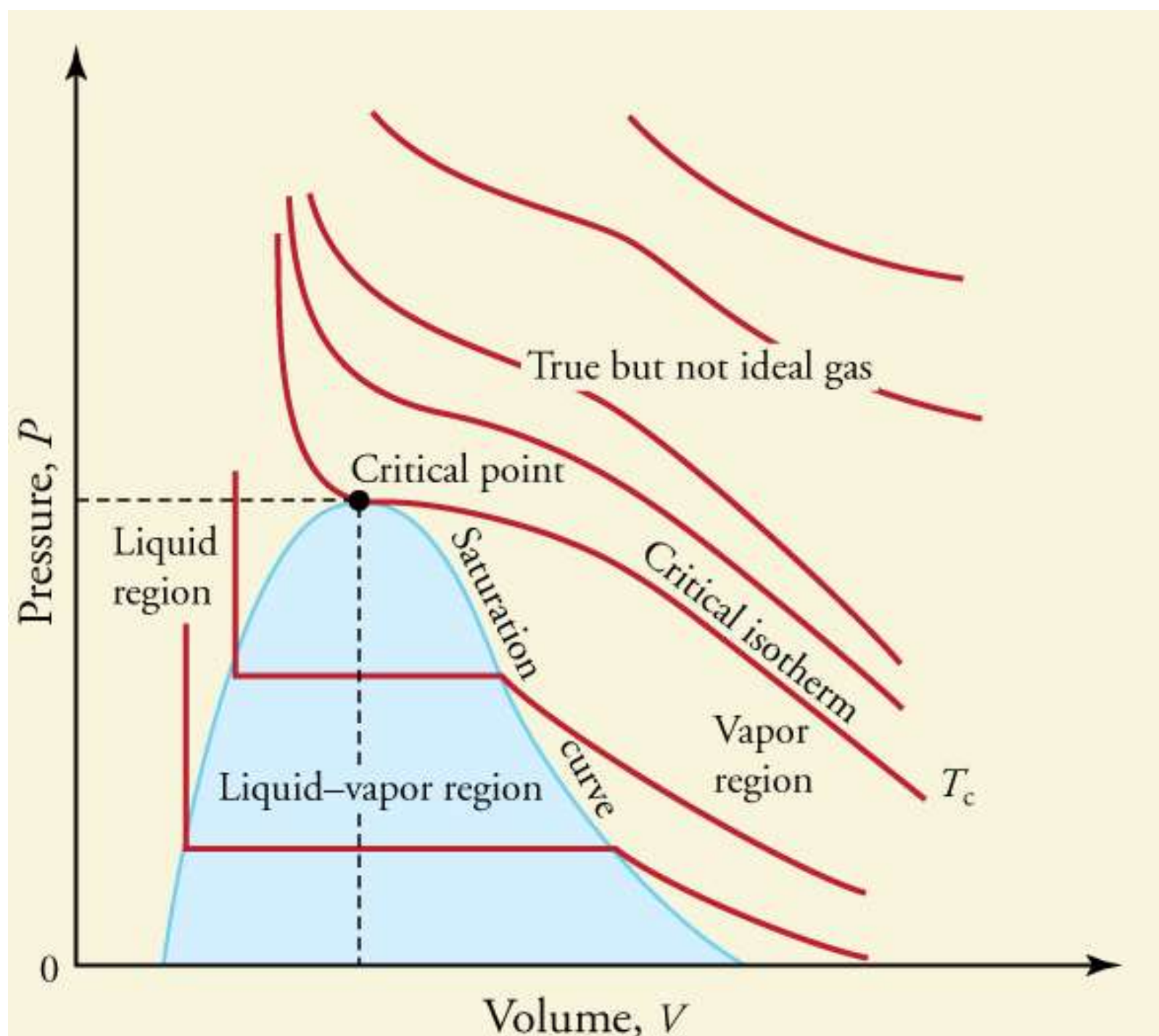
Substance	Critical temperature		Critical pressure	
	K	°C	$\times 10^6$ Pa	atm
Water	647.4	374.3	22.12	219.0
Sulfur dioxide	430.7	157.6	7.88	78.0
Ammonia	405.5	132.4	11.28	111.7
Carbon dioxide	304.2	31.1	7.39	73.2
Oxygen	154.8	−118.4	5.08	50.3
Nitrogen	126.2	−146.9	3.39	33.6
Hydrogen	33.3	−239.9	1.30	12.9
Helium	5.3	−267.9	0.229	2.27

- A phase diagram is *PT* diagram.

- The solid lines are boundaries between phases. Phases coexist on the lines.

- At the triple point, where the lines meet, all three phases exist in equilibrium.
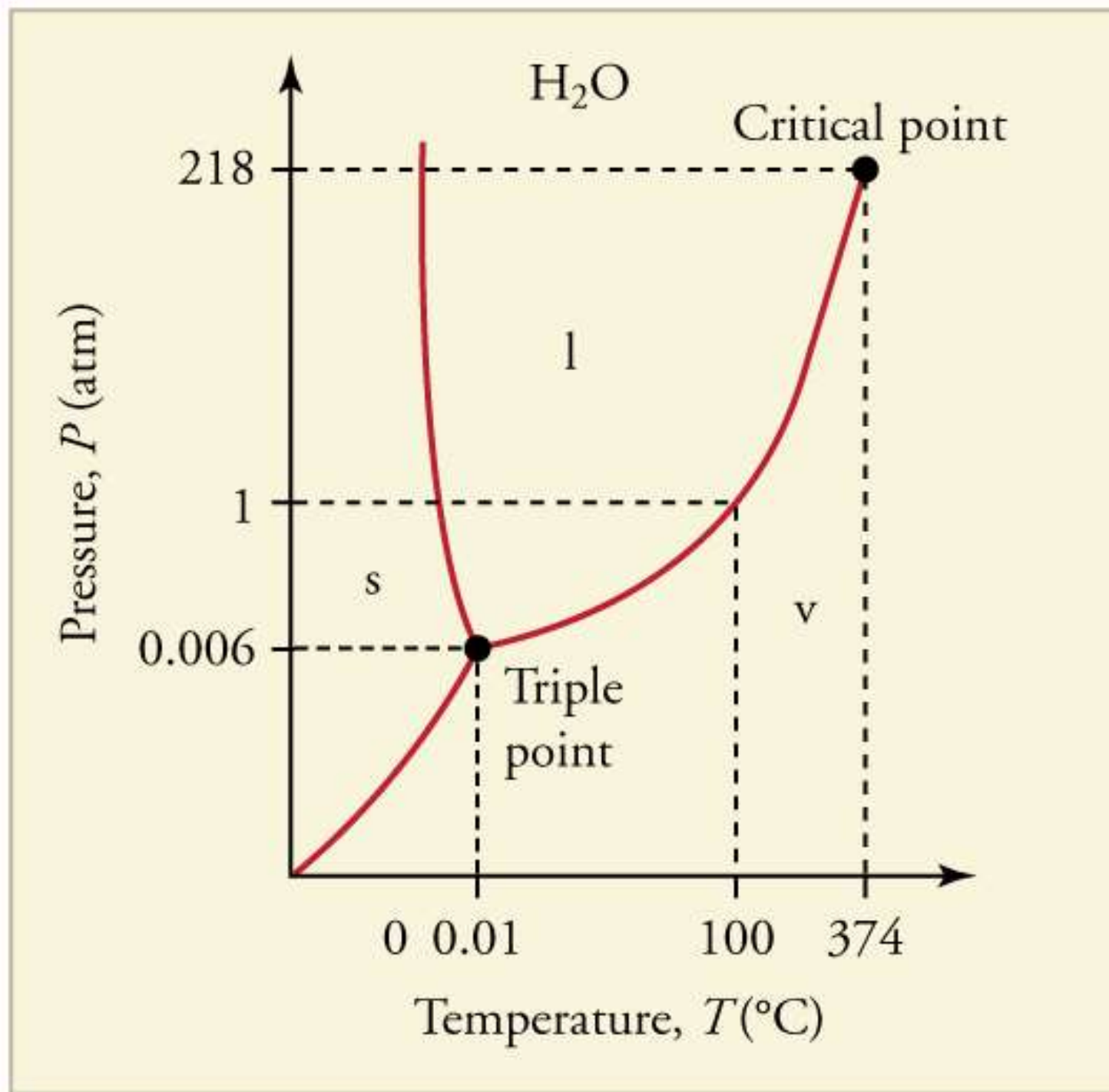
Substance	Triple point temperature		Triple point pressure	
	K	°C	Pa	atm
Water	273.16	0.01	6.10×10^2	0.00600
Carbon dioxide	216.55	−56.60	5.16×10^5	5.11
Sulfur dioxide	197.68	−75.47	1.67×10^3	0.0167
Ammonia	195.40	−77.75	6.06×10^3	0.0600
Nitrogen	63.18	−210.0	1.25×10^4	0.124
Oxygen	54.36	−218.8	1.52×10^2	0.00151
Hydrogen	13.84	−259.3	7.04×10^3	0.0697

- Shown is the phase diagram for water.

- We can see that it boils at 100 °C at 1 atm.

- At pressure ≈ 218 atm, water only boils at ≈ 374 °C. That's the critical point.

- A pressure cooker or covered pot will cook food faster because the water can exist as a liquid at higher temperatures without boiling away.

- At temperatures above the critical, the liquid phase does not exist at any pressure.
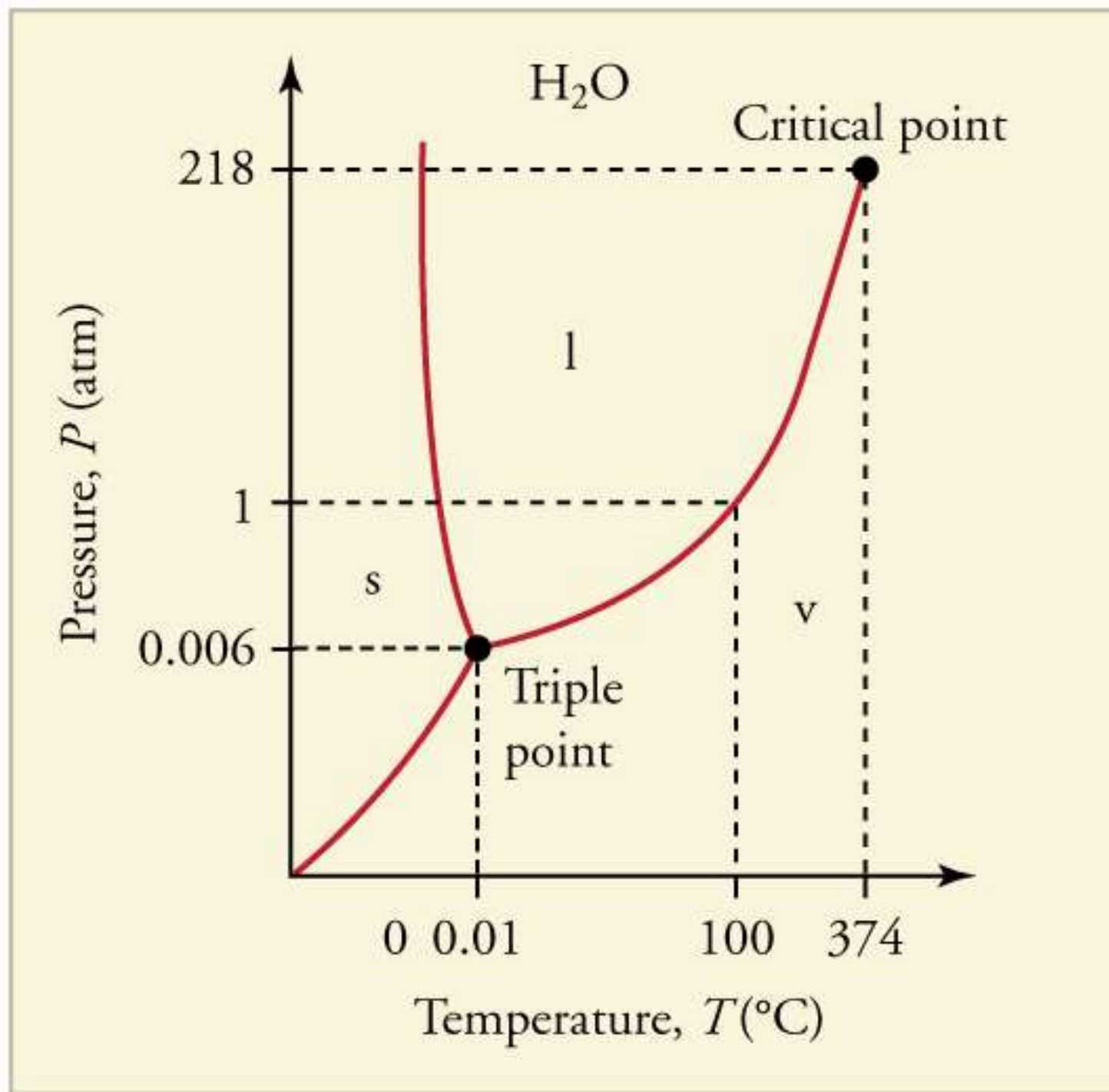
- We also see that water melts at 0 °C at 1 atm.

- When we apply pressure to ice (e.g. with hands or car tires) it decreases the melting temperature.

- At sufficiently low pressures there is no liquid phase.
  - For water, this is <0.00600 atm.

- The phase change directly from solid to gas is called sublimation.
  - E.g.: Solid CO_2, a.k.a. dry ice.
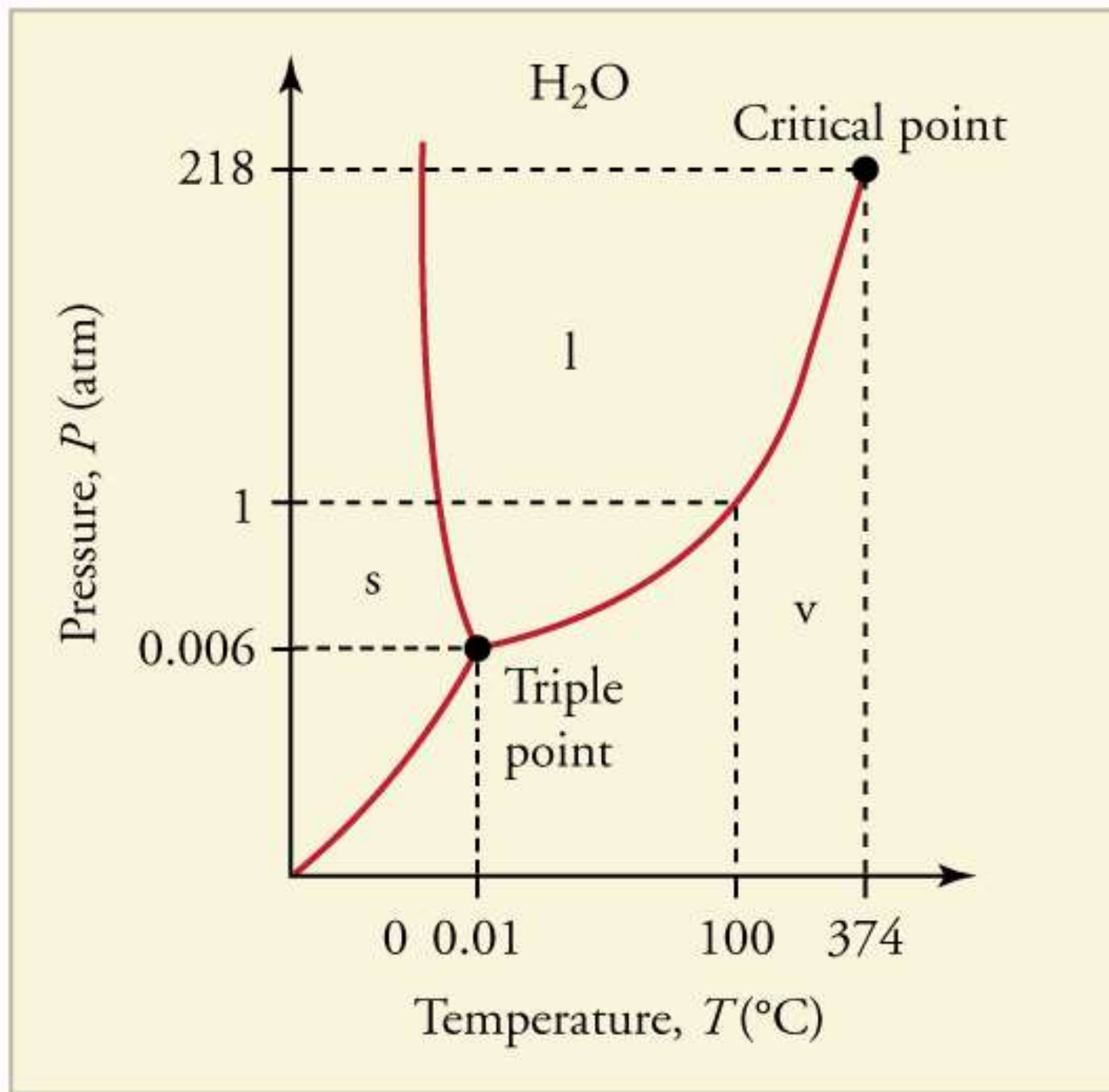
Vapor pressure

- Vapor pressure is the pressure at which a gas exists in equilibrium with its solid or liquid phase.

- It is created by molecules that move fast enough to break away from the liquid or solid and become gas molecules.

- It depends on both the substance and its temperature: larger temperature = larger vapor pressure.

Dalton's law

- Partial pressure is the pressure a gas would create if it occupied the total volume available.

- According to Dalton's law of partial pressures, the total pressure of a mixture of n gases is the sum of partial pressures of each gas:

$$P_{\text{total}} = \sum_{i=1}^{n} P_i = P_1 + P_2 + \cdots + P_n$$

  - This law assumes ideal gas behavior and no chemical reactions between the components.

Simulation

- Simulation for states of matter:

  https://phet.colorado.edu/sims/html/states-of-matter-basics/latest/states-of-matter-basics_all.html