Lecture 5
(Kinetic-Molecular Model)

Physics 161-01 Spring 2012

Douglas Fields

Kinetic-Molecular Model Of an Ideal Gas

- The assumptions of the *kinetic-molecular model* are:

    1. A container contains a very large number of identical molecules.

    2. The molecules behave like point particles that are small compared to the size of the container and the average distance between molecules.

    3. The molecules are in constant motion and undergo perfectly elastic collisions.

   4. The container walls are perfectly rigid and do not move.

Pressure from Collisions

- Let's try to determine the pressure on the walls of a container from the collisions of the molecules. There will be several simplifying assumptions:
  - All molecules of the gas have the same magnitude of velocity in the direction towards the wall, half toward, and half away.
- Then, the momentum change from a collision is just $2mv_x$.
- The number of molecules in a cylinder of height $|v_x|dt$ and area A is just the volume times the density, and half of those are moving towards the wall so:

$$dP_x = \frac{1}{2}\left(\frac{N}{V}\right)\left(A|v_x|dt\right)\left(2m|v_x|\right) = \frac{NAmv_x^2 dt}{V}$$
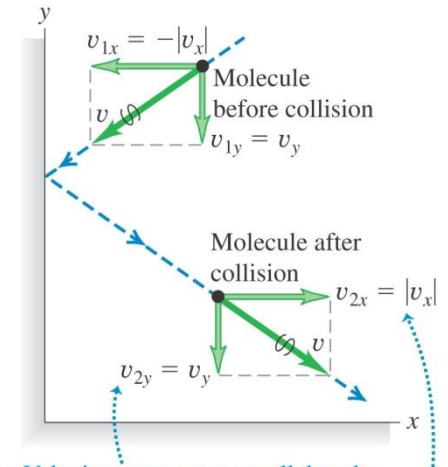
$v_{1x} = -|v_x|$
Molecule before collision
$v_{1y} = v_y$

Molecule after collision
$v_{2x} = |v_x|$

$v_{2y} = v_y$

- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

$|v_x|dt$

A

v_x

Wall

Cylinder: volume $A|v_x|dt$
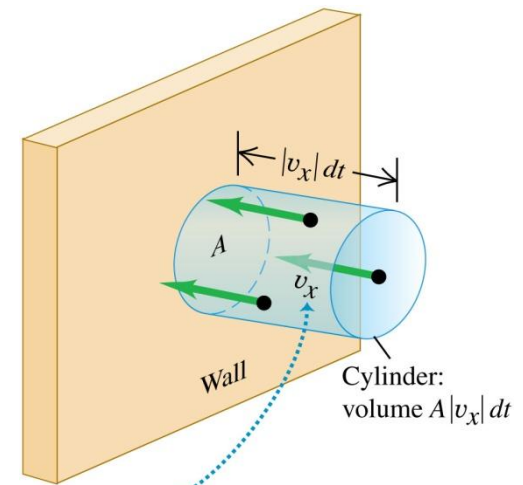
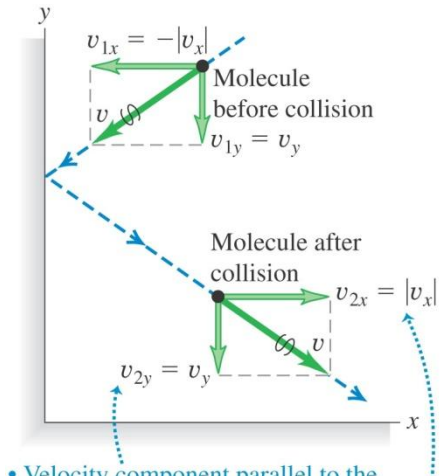All molecules are assumed to have the same magnitude $|v_x|$ of x-velocity.

Pressure from Collisions

$$\frac{dP_x}{dt} = \frac{NAmv_x^2}{V}$$

- But this is the change in momentum per time, or just the force.
- So, we can divide by the area to get the pressure:

$$\frac{dP_x}{dt} = F = \frac{NAmv_x^2}{V} \Longrightarrow$$

$$\frac{F}{A} = p = \frac{Nmv_x^2}{V}$$

$v_{1x} = -|v_x|$

Molecule before collision

$v_{1y} = v_y$

Molecule after collision

$v_{2x} = |v_x|$

$v_{2y} = v_y$

- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

$|v_x|\,dt$

A

v_x

Wall

Cylinder: volume $A|v_x|\,dt$
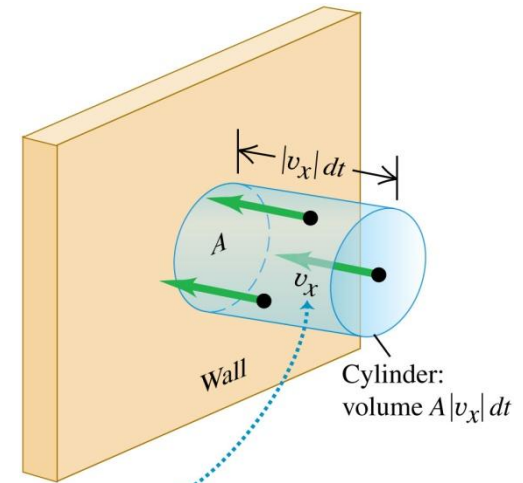
All molecules are assumed to have the same magnitude $|v_x|$ of x-velocity.

Pressure from Collisions

- Now, because each direction can be treated basically the same (since the velocities are high, gravity doesn't matter)
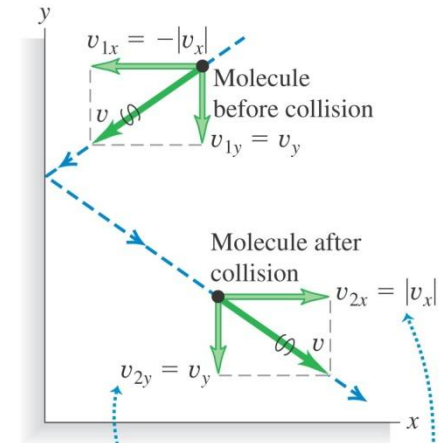
$$\left(v^2\right)_{avg} = \left(v_x^2\right)_{avg} + \left(v_y^2\right)_{avg} + \left(v_z^2\right)_{avg} \Rightarrow$$

$$\left(v_x^2\right)_{avg} = \frac{1}{3}\left(v^2\right)_{avg}$$

- So that the pressure can be related to the average molecular speed:

$$p = \frac{Nmv_x^2}{V} = \frac{1}{3}\frac{Nm\left(v^2\right)_{avg}}{V} = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}m\left(v^2\right)_{avg}\right) \Rightarrow$$

$$pV = \frac{2}{3}N\left(KE_{tr}\right)_{avg} = \frac{2}{3}\left(KE_{tr}\right)$$

$v_{1x} = -|v_x|$ Molecule before collision $v_{1y} = v_y$

Molecule after collision $v_{2x} = |v_x|$

$v_{2y} = v_y$

- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

$|v_x|\,dt$

A

v_x

Wall

Cylinder: volume $A\,|v_x|\,dt$
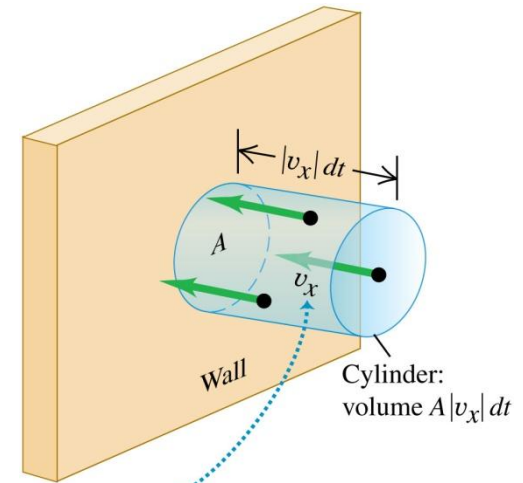
All molecules are assumed to have the same magnitude $|v_x|$ of x-velocity.

Molecular Kinetic Energy and Temperature

- But, if we compare this result to the ideal gas law taken from experiment, then:

$$pV = \frac{2}{3}KE_{tr} = nRT \Rightarrow$$

$$KE_{tr} = \frac{3}{2}nRT$$

- So the temperature times the number of moles is related to the total kinetic energy of the substance, or:

$$KE_{tr} = \frac{3}{2}nRT = \frac{3}{2}\frac{N}{N_A}RT \Rightarrow$$

$$\frac{KE_{tr}}{N} = \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}kT$$

- The average kinetic energy per molecule is directly related to the temperature (k is the Boltzmann constant), as we supposed.

CPS 5-1

Consider two specimens of ideal gas at the same temperature. The molecules in specimen #1 have greater molar mass than the molecules in specimen #2. How do the rms speed of molecules (v_{rms}) and the average translational kinetic energy per molecule (KE) compare in the two specimens?

A. v_{rms} and KE are both greater in specimen #2.

B. v_{rms} is greater in specimen #2; KE is the same in both specimens.

C. v_{rms} is greater in specimen #2; KE is greater in specimen #1.

D. v_{rms} and KE are the same in both specimens.

E. None of the above is correct.

CPS 5-1

Consider two specimens of ideal gas at the same temperature. The molecules in specimen #1 have greater molar mass than the molecules in specimen #2. How do the rms speed of molecules (v_{rms}) and the average translational kinetic energy per molecule (KE) compare in the two specimens?
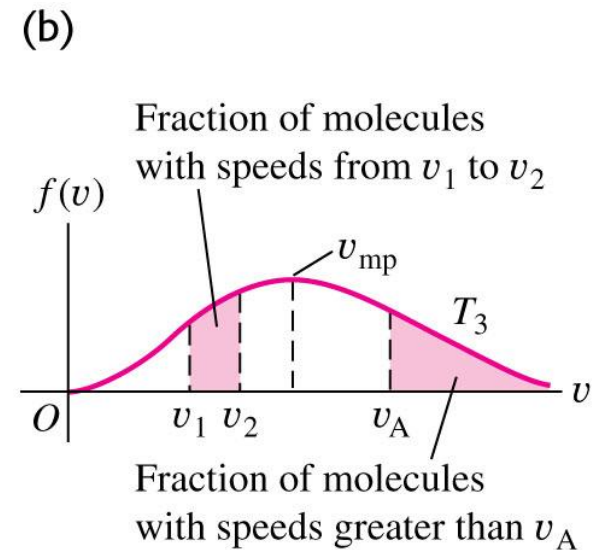
A. v_{rms} and KE are both greater in specimen #2.

B. v_{rms} is greater in specimen #2; KE is the same in both specimens.

C. v_{rms} is greater in specimen #2; KE is greater in specimen #1.

D. v_{rms} and KE are the same in both specimens.

E. None of the above is correct.

Molecular Speeds

- As we have noted, not all molecules have the same speed – there is a distribution of speeds.

- The function that describes these speeds is the Maxwell-Boltzmann distribution:

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

  - Note that: $\int_0^\infty f(v)\,dv = 1$

  - And the average v is greater than the peak value (there is a long tail in the distribution).

(b)

Fraction of molecules with speeds from v_1 to v_2

$f(v)$

v_{mp}

T_3

O v_1 v_2 v_A v

Fraction of molecules with speeds greater than v_A

Molecular Speeds vs. Temperature

- As you raise the temperature of a gas, the distribution becomes broader, and the peak and mean velocities become larger.

- The higher velocity tails of the distribution in liquids are the source of evaporative cooling:

  - High velocity particles are the first to leave the surface, resulting in lower overall average kinetic energies, and thus, lower temperatures.

(a)

$f(v)$

$T_3 > T_2 > T_1$

T_1

T_2

T_3

O

v
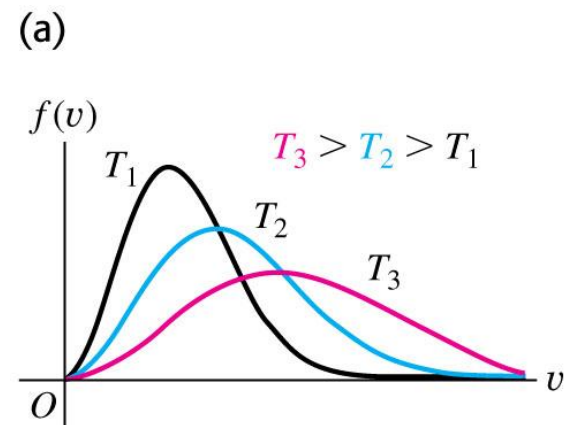
As temperature increases:
- the curve flattens.
- the maximum shifts to higher speeds.

© 2012 Pearson Education, Inc.

Heat Capacities

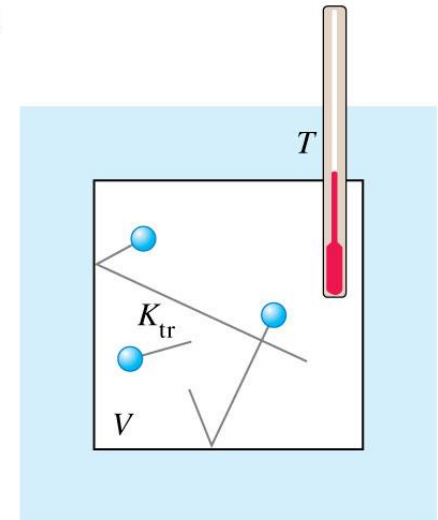- Let us now return to the idea of heat capacity. Recall:

$$Q = nC\Delta T$$

- At constant volume (so that the gas does no work), the heat that enters the system will raise its temperature by raising the average kinetic energy.
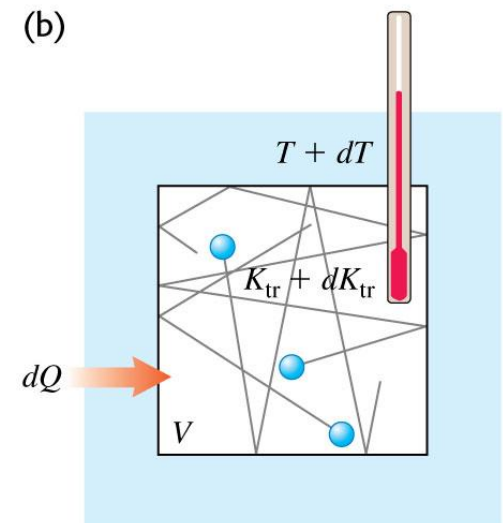
- Then, we have:

$$nC_V dT = \frac{3}{2}nRdT \Rightarrow$$

$$C_V = \frac{3}{2}R$$

Heat Capacity

- This value works well for a monatomic ideal gas, but fails miserably for diatomic and polyatomic gasses…

- Our assumption that all of the heat goes to increasing the average translational kinetic energy must then be wrong.

- Remember, the temperature only depends on the average translational kinetic energy.

Table 18.1 Molar Heat Capacities of Gases

| Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O_2	20.85
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

© 2012 Pearson Education, Inc.

Equipartition of Energy

- It turns out that one of the fundamental principles of physics is the "Equipartition of Energy"

- It states that in thermal equilibrium, energy is shared equally among all of its various forms; for example, the average kinetic energy per degree of freedom in the translational motion of a molecule should equal that of its rotational motions.

- Since we know that:

$$\frac{KE_{tr}}{N} = \frac{3}{2}kT$$

- We know then that at a particular temperature, each "degree of freedom" has

$$\frac{E}{d.o.f} = \frac{1}{2}kT$$

(a) Translational motion. The molecule moves as a whole; its velocity may be described as the x-, y-, and z-velocity components of its center of mass.

We can treat each atom's mass as being located at its nucleus.
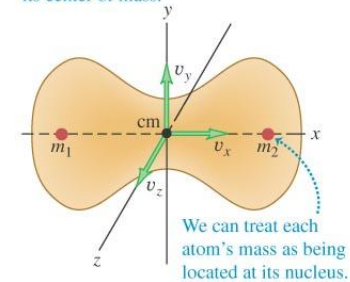
(b) Rotational motion. The molecule rotates about its center of mass. This molecule has two independent axes of rotation.

Independent axes of rotation
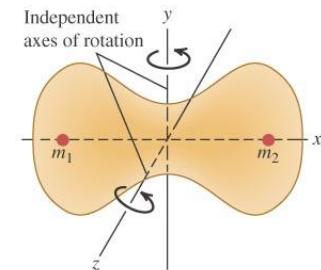
(c) Vibrational motion. The molecule oscillates as though the nuclei were connected by a spring.
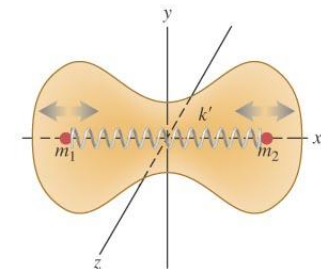
Quantum Effects

- One of the great mysteries of thermodynamics was its failure to reproduce the heat capacities of diatomic gasses (shown below), which turn out to be temperature dependent!
- This was one of the early successes of quantum mechanics.
  - At low temperatures, few of the molecules could reach the excited rotational energy states.
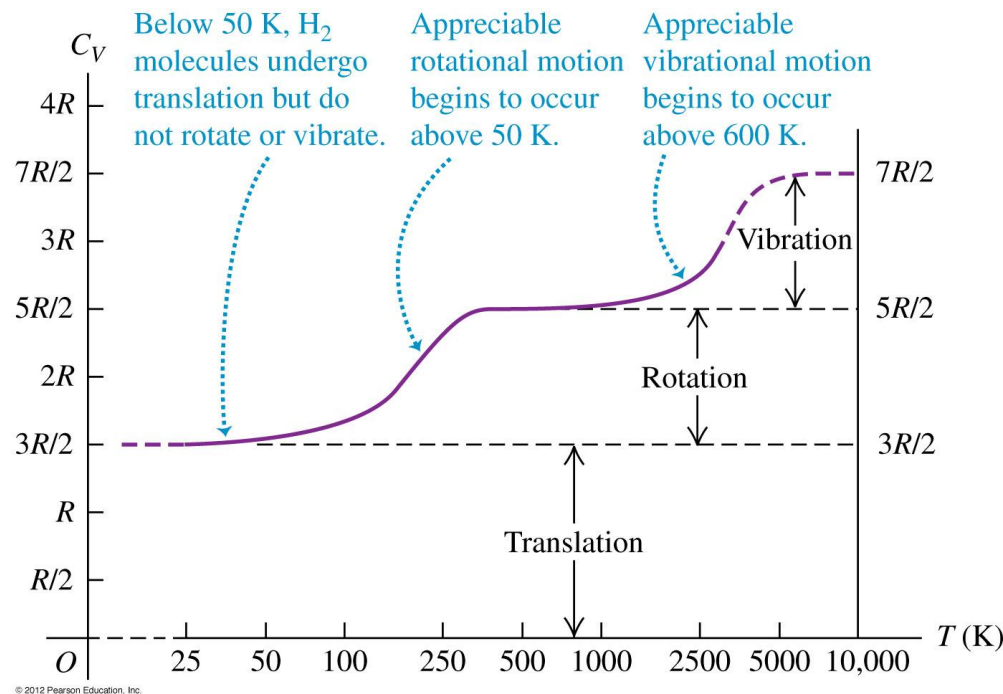
© 2012 Pearson Education, Inc.

CPS 5-2

You have 1.00 mol of an ideal monatomic gas and 1.00 mol of an ideal diatomic gas whose molecules can rotate. Initially both gases are at room temperature. If the same amount of heat flows into each gas, which gas will undergo the greatest increase in temperature?

A. the monatomic gas

B. the diatomic gas

C. Both will undergo the same temperature change.

D. The answer depends on the molar masses of the gases.

CPS 5-2

You have 1.00 mol of an ideal monatomic gas and 1.00 mol of an ideal diatomic gas whose molecules can rotate. Initially both gases are at room temperature. If the same amount of heat flows into each gas, which gas will undergo the greatest increase in temperature?

✓A. the monatomic gas

B. the diatomic gas

C. Both will undergo the same temperature change.

D. The answer depends on the molar masses of the gases.

pVT Diagrams

- A pVT diagram (or block) can give all of the information about a substance's phases.
- Of particular note are the substance's triple point and critical point.
  - Triple point (or line on the block) represents a zone where all three phases of a substance can co-exist.
  - The Critical point is the place, above which there is no phase transition between the liquid and gas phases.
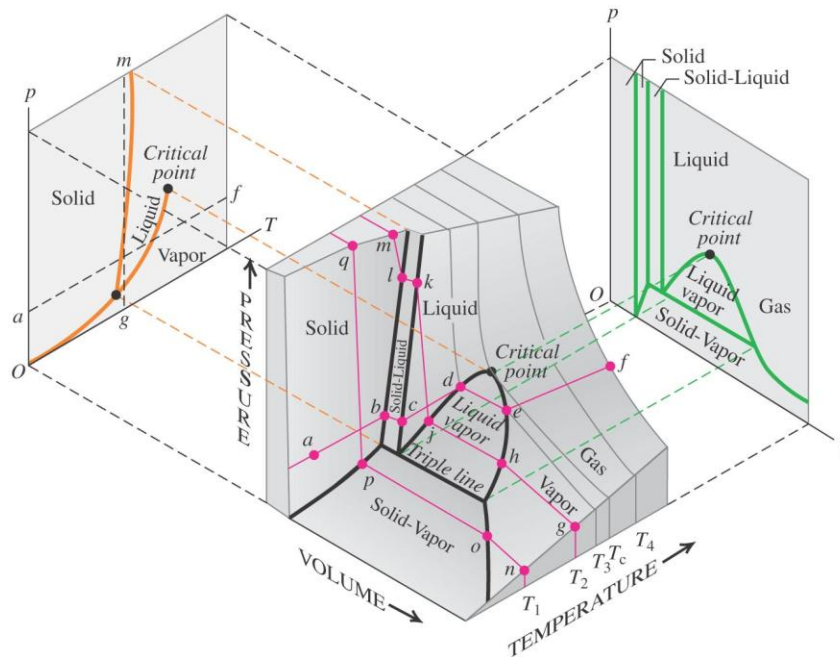
Phase Diagrams

- With some loss of information, it is sometimes easier to see the general trends in a pV or a pT diagram:
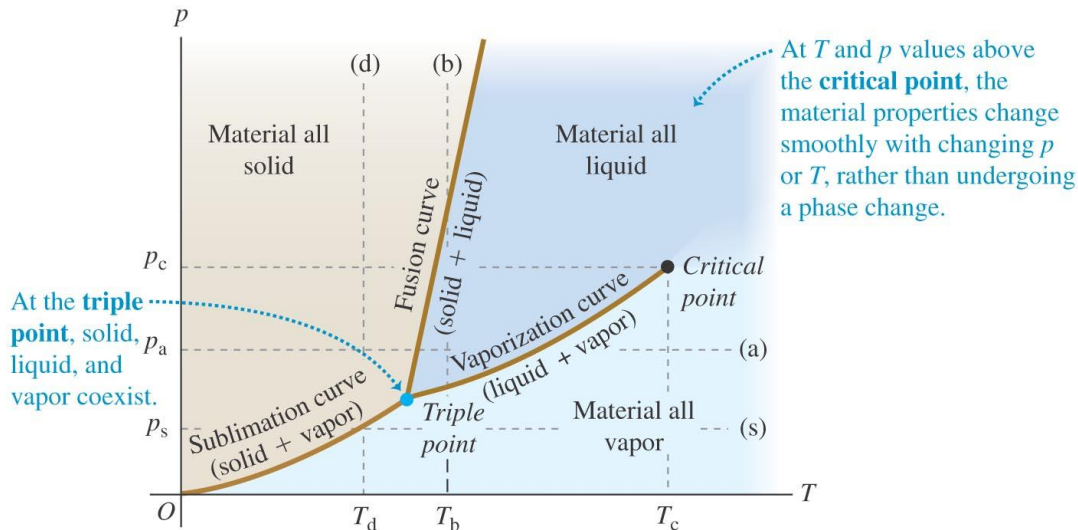
p

(d)   (b)

Material all solid

Material all liquid

Fusion curve

(solid + liquid)

p_c — Critical point

At the **triple point**, solid, p_a liquid, and vapor coexist.

Vaporization curve

(liquid + vapor)

(a)

Sublimation curve

(solid + vapor)

p_s

Triple point

Material all vapor

(s)

O T_d T_b T_c *T*

Table 18.3 Triple-Point Data

Substance	Temperature (K)	Pressure (Pa)
Hydrogen	13.80	0.0704×10^5
Deuterium	18.63	0.171×10^5
Neon	24.56	0.432×10^5
Nitrogen	63.18	0.125×10^5
Oxygen	54.36	0.00152×10^5
Ammonia	195.40	0.0607×10^5
Carbon dioxide	216.55	5.17×10^5
Sulfur dioxide	197.68	0.00167×10^5
Water	273.16	0.00610×10^5

pVT Diagram for Ideal Gases