# Chapter 18
# Thermal Properties of Matter

In this section we define the thermodynamic *state variables* and their relationship to each other, called the *equation of state.* The system of interest (most of the time) is a "closed" container of gas. Once we define the properties of this closed container of gas, we will explore its interaction with the surrounding "environment" by developing the *first law* of thermodynamics (Ch. 19), and the *second law* of thermodynamics (Ch. 20).

## 1 Equations of State

Let's define the "state variables" of a thermodynamic system.

1. $P$ the pressure [Pa]
2. $V$ the volume $[m^3]$
3. $T$ the temperature $[K]$
4. $n$ the no. of moles $[mol]$
   or $N$ the no. of constituent particles $[no.]$
5. $S$ the entropy $[J/K]$

Another useful quantity describing the gas is its mass which can be determined from the number of *moles* ($n$), and the *molecular weight* ($M$), or the *molar mass..*

$$\text{mass} = n\,M$$

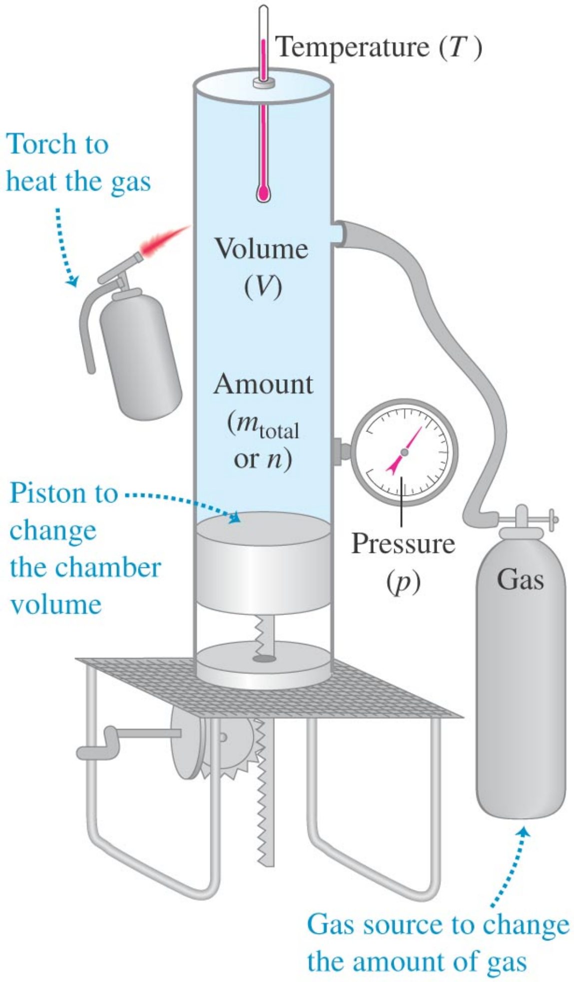
From experiment, we observe the following relationships between the *pressure*, the *volume*, the number of *moles*, and the *temperature.*

$$P \sim T \qquad P \sim n \qquad \text{and} \quad P \sim \frac{1}{V}$$

These can be combined into a single relationship as follows:

$$P \sim \frac{nT}{V} \qquad \text{or} \qquad PV = nRT \qquad \text{(the ideal gas law)}$$

where $R$ is the *universal gas constant* (8.31 J/(mol·K) ).



**Ex. 3** A cylindrical tank has a tight-fitting piston that allows the volume of the tank to be changed. The tank originally contains 0.110 $\text{m}^3$ of air at a pressure of 0.355 atm. The piston is slowly pulled out until the volume of the gas is increased to 0.390 $\text{m}^3$. If the temperature remains constant, what is the final value of the pressure?

**Ex. 9** A large cylindrical tank contains 0.750 $\text{m}^3$ of nitrogen gas at $27^o$C and $7.50 \times 10^3$ Pa (absolute pressure). The tank has a tight-fitting piston that allows the volume to be changed. What will be the pressure if the volume is decreased to 0.410 $\text{m}^3$ and the temperature is increase to $157^o$C?

## 1.1 The Van Der Waals Equation

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The constants $a$ and $b$ are empirical constants, and are different for different gases. The constant $b$ represents the volume of a *mole* of molecules while the constant $a$ depends on the attractive intermolecular forces, which reduce the pressure of the gas for given values of $n$, $V$, and $T$ by *pulling* the molecules together as they *push* against the walls of the container. If $n/V$ is small, you return to the ideal gas law.

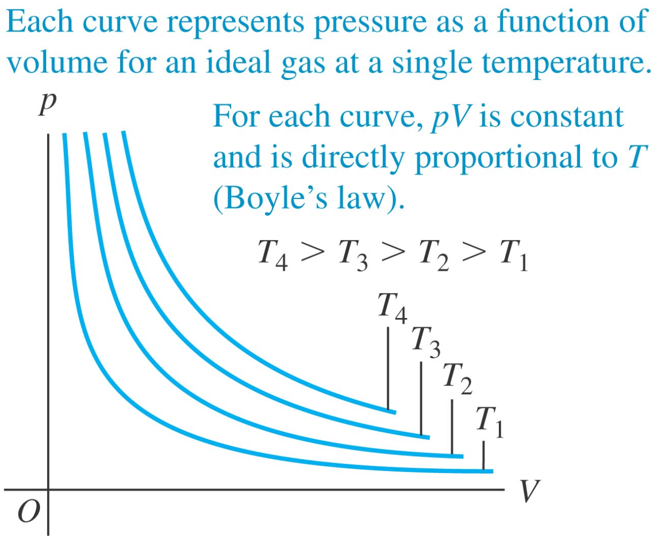
## 1.2 pV-Diagrams

We will be using the $pV$ diagram on a regular basis throughout the next chapter when we study heat engines and refrigerators.

If you know the pressure $P$, the volume $V$, and the number of moles of gas $n$ in the *system*, then there is a unique temperature for the system.

$$T = \frac{PV}{nR}$$

By keeping the temperature constant, and varying the pressure and volume, we can trace out a *curved*, hyperbolic line on the $pV$ diagram called on *isotherm*.


Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

For each curve, $pV$ is constant and is directly proportional to $T$ (Boyle's law).

$T_4 > T_3 > T_2 > T_1$

## 2 Molecular Properties of Matter

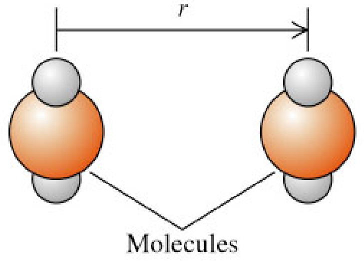
One mole contains **Avogadro's number** of particles (e.g., atoms or molecules).

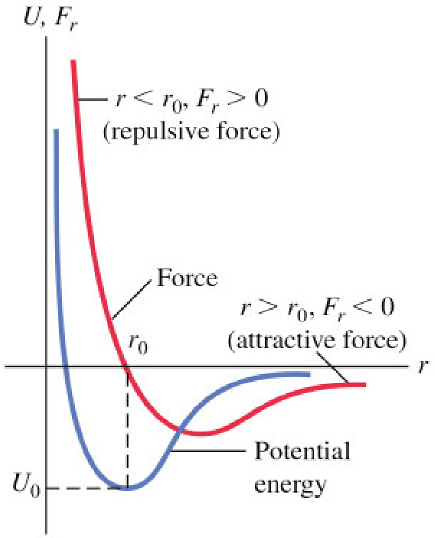
$$N_A = 6.022 \times 10^{23} \text{ molecules/mol} \qquad \text{(Avogadro's number)}$$

The mass per molecule (or atom) $m$ is:

$$m = \frac{M}{N_A}$$

where $M$ is the *molecular mass* in kg/mol.





**Ex. 23** **How Close Together Are Gas Molecules?** Consider an ideal gas at $27^o$C and 1.00 atm. To get some idea how close these molecules are to each other, on the average, imagine them to be uniformly spaced, with each molecule at the center of a small cube. (a) What is the length of an edge of each cube if adjacent cubes touch but do not overlap? (b) How does this distance compare with the diameter of a typical molecule? (c) How does their separation compare with the spacing of atoms in solids, which typically are about 0.3 nm apart?

# 3 Kinetic-Molecular Model of an Ideal Gas

In this section we start our investigation of the macroscopic properties of a gas by studying its microscopic interactions.

### Properties of the Ideal Gas

1. The ideal gas consists of particles, which are in random motion and obey Newton's laws of motion.
2. The total number of molecules is "large."
3. The volume occupied by the molecules is a negligibly small fraction of the volume occupied by the gas.
4. No forces act on a molelcule except during a collision, either with the container walls or with another molecule.
5. All collisions are *(i) elastic* and *(ii) of negligible duration.*

### A Molecular View of Pressure

Consider a cubical box of edge $L$ containing an ideal gas. The force of an individual molecule of mass $m$ with momentum $p_x = mv_x$ on a single wall can be written as:

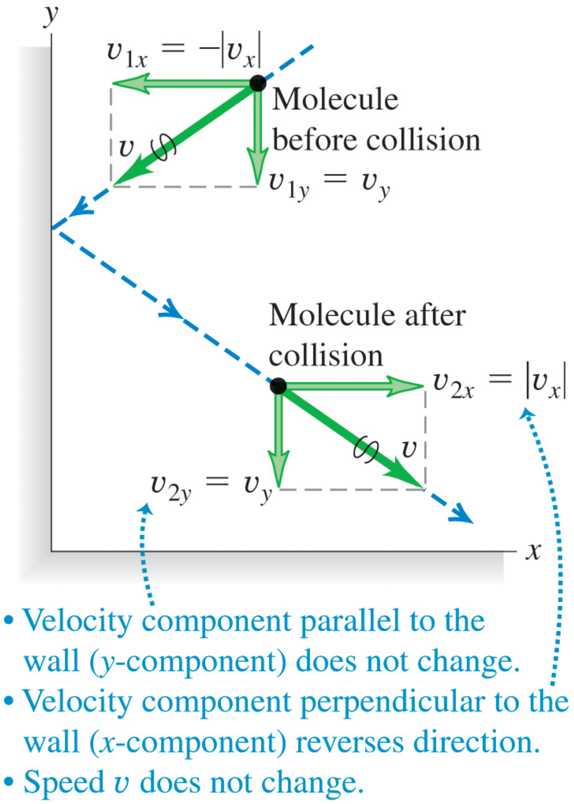
$$F_x = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

The pressure due to $N$ molecules is defined to be $F/A$ where $F = \sum_{i=1}^{N} F_{xi}$, so we can write:

$$p = \frac{F}{A} = \frac{1}{L^2}\,\frac{mv_{1x}^2 + mv_{2x}^2 + \cdots}{L} = \frac{m}{L^3}\left(v_{1x}^2 + v_{2x}^2 + \cdots\right)$$

Using the relationship $Nm/L^3$ is the density $\rho$, we can write:

$$p = \rho\left(\frac{v_{1x}^2 + v_{2x}^2 + \cdots}{N}\right) = \rho\left(v_x^2\right)_{\text{av}}$$



- 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.

Figure 1: Figure 18.11 from University Physics 15th edition.

For any molecule, we can write the speed-squared as $v^2 = v_x^2 + v_y^2 + v_z^2$, such that $v_x^2 = v_y^2 = v_z^2 = \frac{1}{3}v^2$. Now we can write the above equation as:

$$p = \frac{1}{3}\rho(v^2)_{\text{av}} \tag{1}$$

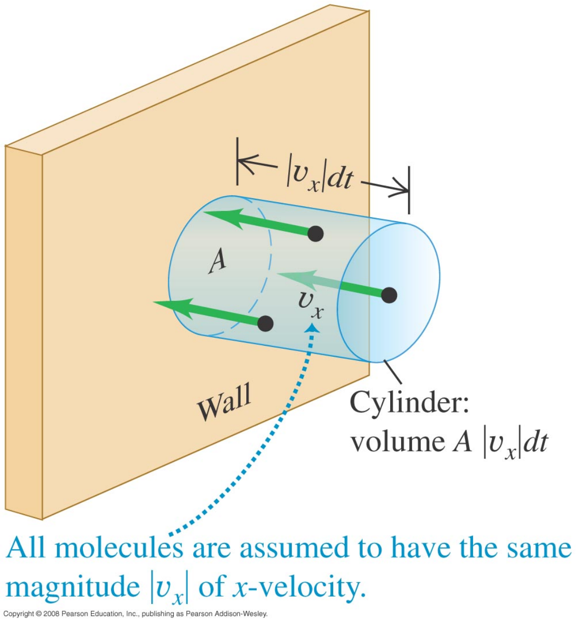


Figure 2: Figure 18.12 from University Physics 15th edition.

We define a new velocity, the *root-mean-square* velocity $v_{\text{rms}}$ to be the average speed of the molecules between collisions:

$$v_{\text{rms}} = \sqrt{\frac{3p}{\rho}} \tag{2}$$

Notice that the pressure $p$ of a gas varies proportional to the $v_{\text{rms}}^2$.

**The average translational kinetic energy per molecules** $K_{trans}$

$$K_{\text{tot}} = \frac{1}{2}mv_{rms}^2N \qquad \text{(for } N \text{ molecules)}$$

$$v_{\text{rms}}^2 = 3p\left(\frac{V}{Nm}\right) \qquad pV = \frac{N}{3}mv_{\text{rms}}^2 \qquad pV = \frac{2N}{3}\left(\frac{1}{2}mv_{\text{rms}}^2\right)$$

$$pV = \frac{2}{3}N\left(K_{\text{trans}}\right)$$

where $K_{\text{trans}}$ is the average *kinetic energy* for a single molecule ($\frac{1}{2}mv_{\text{rms}}^2$). Recall that the ideal gas law states:

$$pV = nRT \qquad \text{(the Ideal Gas Law)}$$

$$K_{\text{trans}} \;=\; \frac{3}{2}\frac{(pV)}{N} \;=\; \frac{3}{2N}\,(nRT) \;=\; \frac{3}{2}\,kT \qquad \text{(for a single molecule)} \tag{3}$$

where $k = 1.38 \times 10^{-23}$ J/K, the *Boltzmann constant*, and $N/n = N_A$, and $R/N_A = k$.

The total energy of the gas is:

$$K_{\text{tot}} \;=\; N\,K_{\text{trans}} \;=\; \frac{3}{2}NkT \qquad \text{(for } N \text{ molecules)} \tag{4}$$

or

$$K_{\text{tot}} \;=\; \frac{3}{2}nRT \qquad \text{(for } n \text{ moles)}$$

Finally, we can relate the average speed between collisions ($\sqrt{v_{\text{rms}}^2}$) to the temperature $T$ and mass $m$ using Eq. 3.

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \qquad \text{(root-mean-square velocity of a gas molecule)} \tag{5}$$

Likewise, we have two forms for writing the equation of state:

$$\begin{array}{ccc} pV \;=\; nRT & \text{and} & pV = NkT \\ \text{(macroscopic)} & & \text{(microscopic)} \end{array}$$

**Ex. 29** A deuteron, ${}^2_1$H, is the nucleus of a hydrogen isotope and consists of one proton and one neutron. The plasma of deuterons in a nuclear fusion reactor must be heated to about 300 million K. What is the rms speed of the deuterons? Is this a significant fraction of the speed of light ($c = 3.0 \times 10^8$ m/s)? (b) What would the temperature of the plasma be if the deuterons had an rms speed equal to 0.10c?

### 3.1 Collisions Between Molecules

Up until now, we've assumed that molecules are point-like objects. Let's consider a more realistic model in which the molecules are rigid spheres with radius $r$. Let's assume a system where we have $N$ molecules in a fixed volume $V$. The *mean-free-path* between collisions can be written as:

$$\lambda = \frac{V}{4\pi\sqrt{2}\,r^2 N} \qquad \text{(the mean free path of a gas molecule)} \tag{6}$$

Likewise, we can use the *microscopic* form of the ideal gas law ($pV = NkT$) and write Eq. 6 as:

$$\lambda = \frac{kT}{4\pi\sqrt{2}\,r^2 p} \tag{7}$$

## 4 Heat Capacities

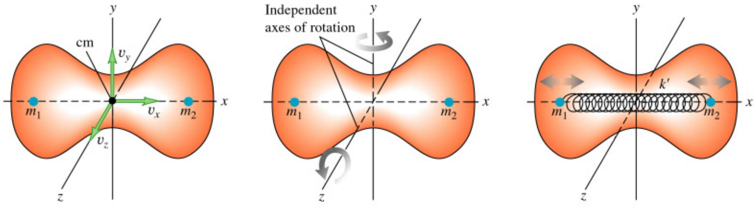
When we add heat to a system, we are increasing its molecular *kinetic* energy. If we hold the volume $V$ constant for a *monatomic* ideal gas, we can write that the change in KE is equal the heat exchanged $Q$. Heat is *energy* in transit. We don't say that a system "contains so much heat." Instead, $Q$ is a measure of the thermal energy flowing *in* or *out* of a system. This can be written as:

$$dK = dQ \qquad \Rightarrow \qquad \frac{3}{2}nR\,dT = n\,C_{\mathrm{V}}\,dT \tag{8}$$

where $C_{\mathrm{V}}$ is the *molar specific heat* at constant volume. Comparing the two sides of Eq. 8 we can find the value for $C_{\mathrm{V}}$ for a monatomic gas.

$$C_{\mathrm{V}} = \frac{3}{2}R = 12.47\,\mathrm{J/mol\cdot K} \qquad \text{(for a monatomic gas)}$$

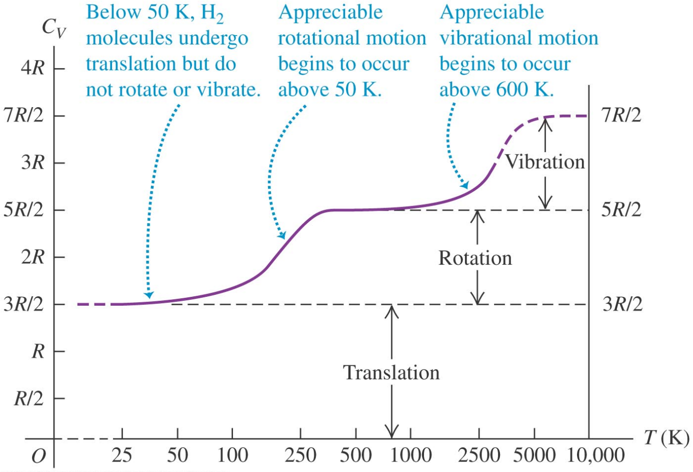
There's a famous theorem in statistical physics that says the value of $C_{\mathrm{V}}$ increases by $\frac{1}{2}R$ for every degree of freedom. If we consider a gas consisting of diatomic molecules at *ordinary* temperatures, it's possible to induce rotational



(a) Translational motion (b) Rotational motion (c) Vibrational motion

motion around two of the three axes, thus adding one unit of $R$ to the value of $C_{\mathrm{V}}$.

$$C_{\mathrm{V}} = \frac{5}{2} R = 20.79\,\mathrm{J/mol \cdot K} \qquad \text{(for a diatomic gas, including rotations)}$$



Below 50 K, $H_2$ molecules undergo translation but do not rotate or vibrate.

Appreciable rotational motion begins to occur above 50 K.

Appreciable vibrational motion begins to occur above 600 K.

## 5 Molecular Speeds

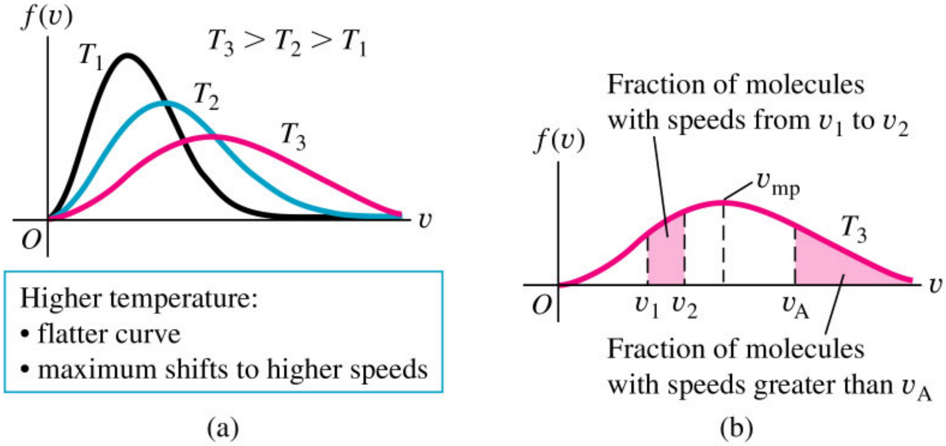
If we have a system containing $N$ molecules at a temperature $T$, then the number of molecules $dN$ with velocity in the range between $v$ and $v + dv$ is given by:

$$dN = N f(v)\, dv$$

where $f(v)$ is the probability per unit speed interval ($v \to v + dv$).

## 5.1 The Maxwell-Boltzman velocity distribution

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \tag{9}$$



### 5.1.1 The most probable velocity

$$\frac{\partial f(v)}{\partial v} = 0 \qquad \text{and solve for } v_{\text{mp}}$$

$$v_{mp} = \sqrt{\frac{2kT}{m}} \tag{10}$$

### 5.1.2 The average velocity

$$v_{\mathrm{av}} = \int_0^\infty v\, f(v)\, dv$$

$$v_{\mathrm{av}} = \sqrt{\frac{8kT}{\pi m}} \tag{11}$$

### 5.1.3 The root-mean-square velocity

$$\left(v^2\right)_{\mathrm{av}} = \int_0^\infty v^2\, f(v)\, dv$$

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}} \tag{12}$$

This result agrees with the equipartition theorem and the results we derived earlier.

Here is a Mathematica program that investigates the properties of the Maxwellian velocity distribution.

**Ex. 41** For polyatomic carbon dioxide gas ($CO_2$, molar mass 44.0 g/mol) at $T = 300$ K calculate (a) the most probable speed $v_{\mathrm{mp}}$; (b) the average speed $v_{\mathrm{av}}$; (c) the root-mean-square speed $v_{\mathrm{rms}}$.

# 6 Phases of Matter

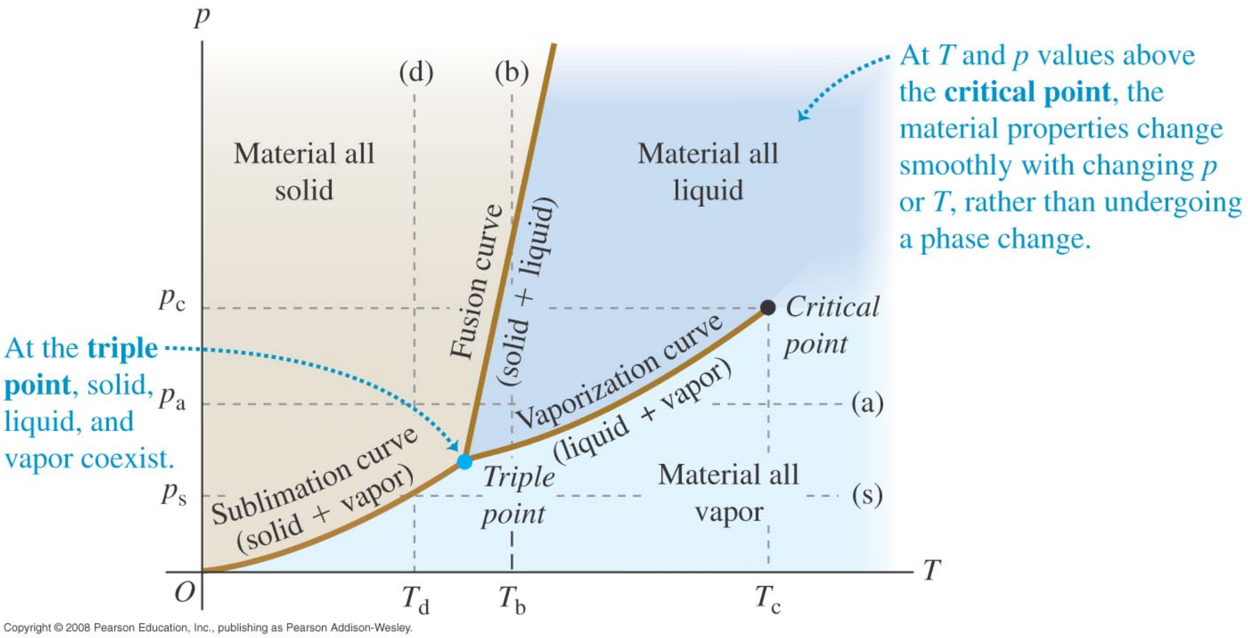


Figure 3: A typical $p$-$T$ diagram depicting the phase transitions for most materials. Beyond the "critical point" the substance is referred to as a **supercritical fluid**. There is no longer a phase transition between vapor and liquid. This is where the liquid and gaseous phases of the substance merge into a single phase, and where distinct liquid and gas phases do not exist. The supercritical fluid can effuse through solids like a gas, and dissolve materials like a liquid.