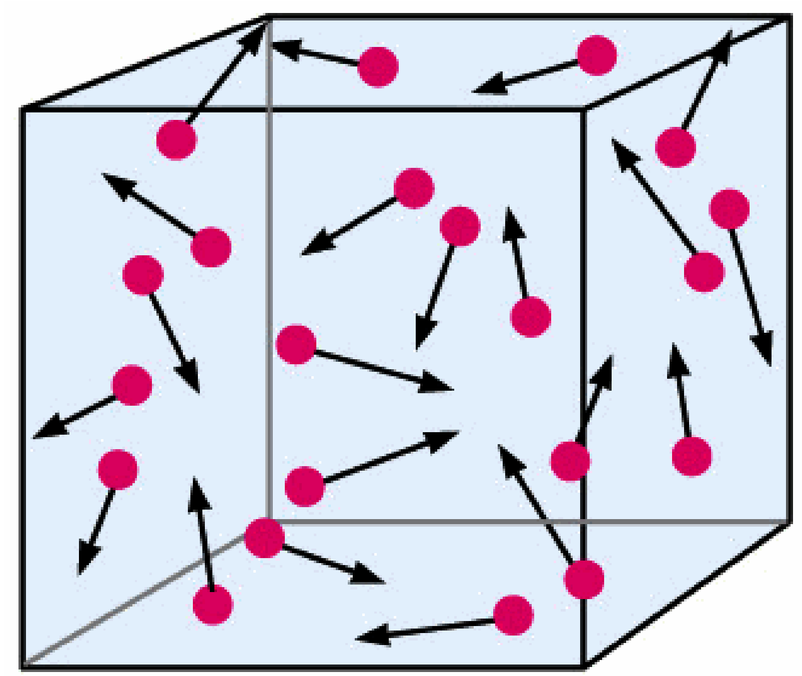
Thermal Properties of Matter



A volume is filled with a mixture of several different gases. Some are monatomic, some are diatomic. Some particle masses are large, some are small. Which quantities are the same for each of the gases present?

1. pressure
2. temperature
3. internal energy
4. both 2 and 3
5. all of the above
6. need more information

ANS: **2**—only the temperature is the same for all gases.

All component gases are the same because they quickly come to thermal equilibrium after they mix, which means they will be at the same temperature.

The gases do not have to have the same pressures. We know that the temperatures and volumes will be equal. Therefore, the "partial pressure" of each gas will depend on the amount of that gas in the container: $P = (k_B T/V)N$, where the quantity in parentheses is the same for all gases.

On a molecular level, recall that the pressure on a wall depends partly on the number of molecules that hit in a certain amount of time. Gases with a small number of molecules have fewer collisions than gases with a large number of molecules.

Finally, while the average translational kinetic energy is the same for all molecules, $(3/2)k_B T$, the total energies of the different gases can differ. Again, this is because there may be different amounts of each gas in the total, and different degrees of freedom per molecule for the different gases.

A volume is filled with a mixture of several different gases. Some are monatomic, some are diatomic. Some particle masses are large, some are small. Which quantities are the same for all of the molecules present?

1. average speed
2. average total energy
3. average translational kinetic energy
4. both 2 and 3
5. all of the above
6. need more information

ANS: 3—only the average translational kinetic energy is the same for all of the molecules.

As I mentioned before, all of the gases have the same temperature. They all have the same average translational kinetic energy per molecule, $(3/2)k_B T$, because they all have three translational degrees of freedom. However, because the molecules may have different masses, they may have different average speeds. They also may have different total energies per molecule because there may be different numbers of degrees of freedom. Diatomic and polyatomic molecules will likely have rotational kinetic energy in addition to the translational kinetic energy. If the temperature is great enough, they also may have vibrational energy. The molecules with more degrees of freedom will have a greater total energy on average.

Warmup Question

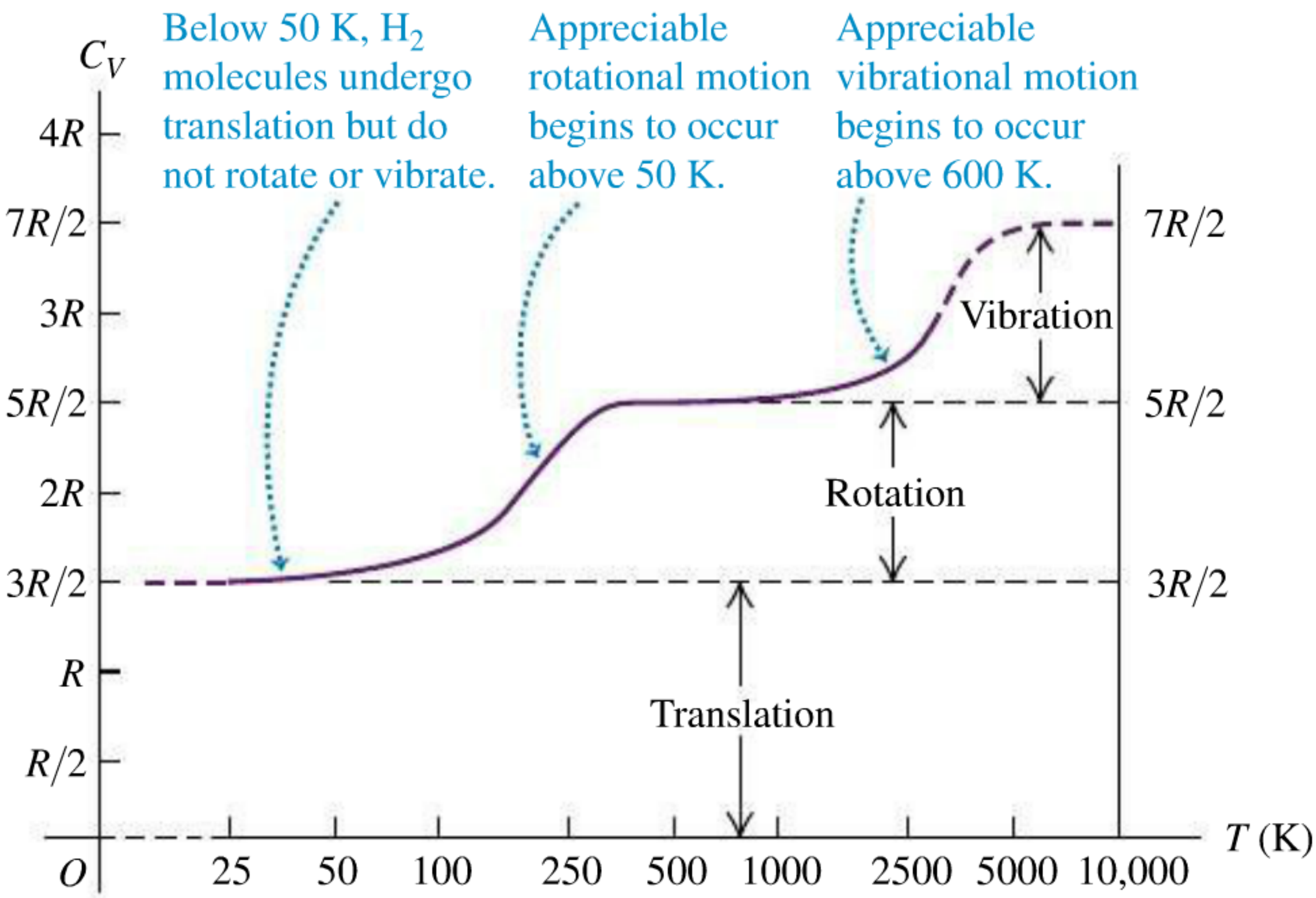
For two gases of different composition in thermal equilibrium, what do their particles share in common?

1. Average translational speed
2. Average translational energy per molecule
3. Average total energy per molecule
4. Molar heat capacity
5. All of the above
6. None of the above

ANS: **2**—The average translational energy per molecule will be the same for both gases.

The objects have the same temperature, so they will have the same average translational kinetic energy per molecule, $(3/2)k_B T$. They will not have the same average (rms) speed unless they have the same mass per molecule. The will not have the same average total energy per molecule because gases of different composition have different degrees of freedom. This is also the reason they will not have the same molar heat capacity.

Molar Heat Capacity of a Diatomic Gas



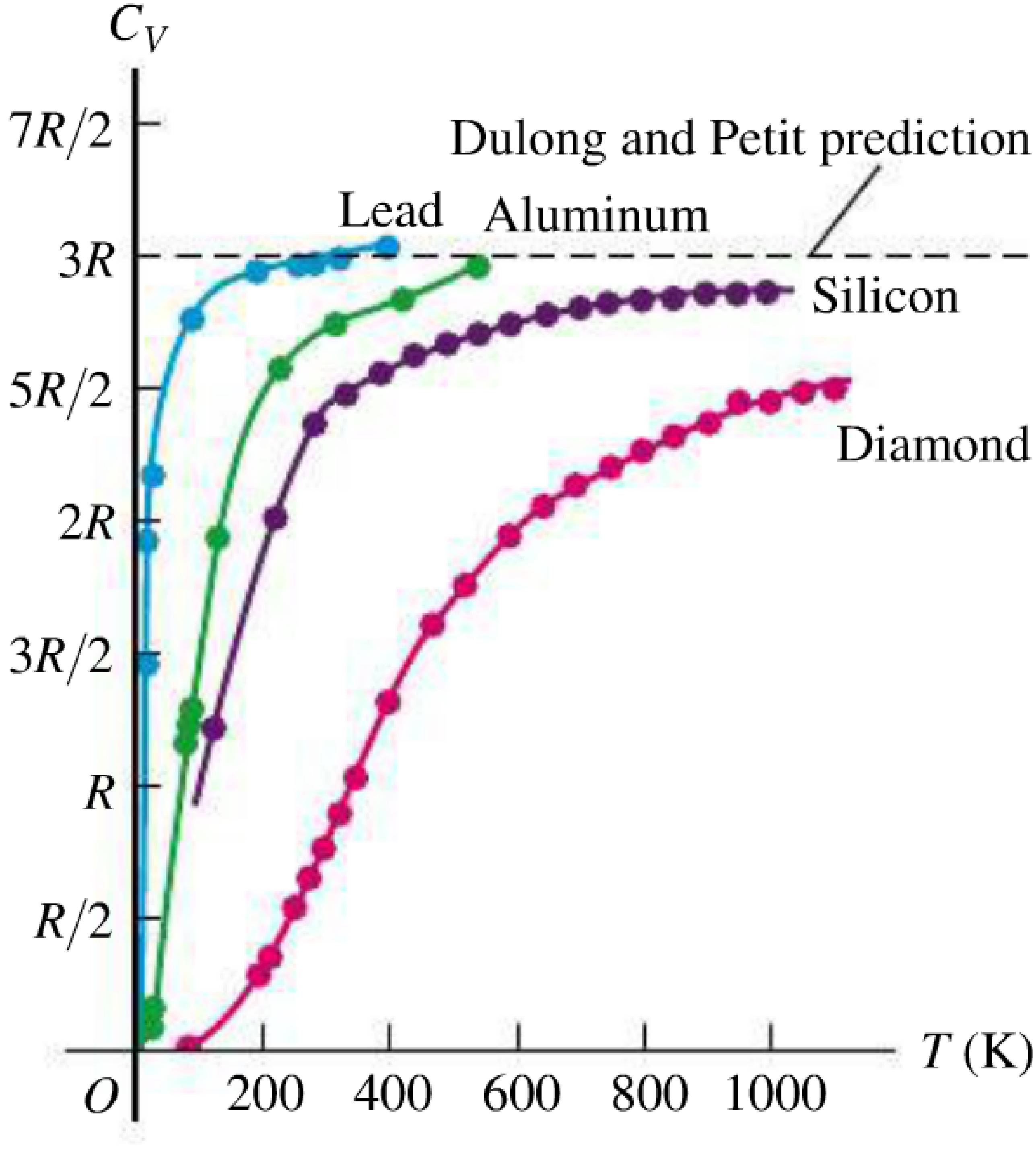
ANS: The graph on the previous page is a sketch of the molar heat capacity of a diatomic gas as a function of temperature.

Gas molecules are always free to move in three dimensions of space, so they will always have three translational degrees of freedom. Even as temperatures approach absolute zero, this motion won't stop, so the molar heat capacity of an ideal gas will always be, at minimum, $C_V = \frac{3}{2}R$, if such a gas could even exist at that temperature (they can't).

Diatomic molecules will have a maximum of two rotational degrees of freedom. Due to quantum physics, these rotations don't activate until enough energy is available. Therefore, we don't see evidence of these rotations at low temperatures, but do see them at higher temperatures, at around room temperature and higher. At intermediate temperatures some, but not all, of the molecules will exhibit rotation, so we see the molar heat capacity gradually rise from $C_V = \frac{3}{2}R$ to $C_V = \frac{5}{2}R$.

Diatomic molecules can also vibrate along their bond. This one available mode of vibration corresponds to two vibrational degrees of freedom. The activation energy for these vibrations is even greater, so we do not see them until we reach very high temperatures. Eventually, the molar heat capacity of a diatomic gas will rise to $C_V = \frac{7}{2}R$, with a transition as more molecules begin to vibrate.

Molar Heat Capacity of a Solid



ANS: The graph on the previous page shows experimental values for the molar heat capacity of different solid materials as a function of temperature.

In the simplest possible model, solids are a collection of molecules bound together with spring-like binding forces that hold them in place. The molecules are not free to move so, unlike for a gas, they have no translational degrees of freedom. The molecules are not free to rotate in place, so they have not rotational degrees of freedom.

However, the molecules can oscillate in place along three dimensions. These three modes of vibration correspond to a total of six degrees of freedom. At high temperatures, we expect these degrees of freedom to be available to the solid, so the molar heat capacity of a solid should be $C = \frac{3}{2}R$. This is the **law of Dulong and Petit**. For high temperatures, all solids obey this law pretty well.

At low temperatures, however, not all degrees of freedom will be turned on. Some molecules will vibrate, while others will not. In the limit $T \to 0$ we expect the heat capacity to go to zero as molecular vibrations stop.

Between absolute zero and higher temperatures, we expect a non-zero heat capacity as the additional heat activates more, but not yet all, molecular vibrations. This is what we see in the diagram above. The different materials have different intermolecular bond strengths, so we expect different energies to excite the vibrational modes.

Two gases in identical containers with fixed volumes have the same pressures and number of moles. They are both monatomic, but the atoms of one gas are twice as massive as the other. You add the same amount of heat to both. Which gets hotter?

1. the gas with the heavier atoms
2. the gas with the lighter atoms
3. both reach the same temperature
4. more information is needed

ANS: 3—both reach the same temperature.

All of the molecules start out at same temperature. The volumes are fixed, so any heat added to the gases simply adds to the total thermal energy, increasing the energy per molecule. Because the molecules have the same number of degrees of freedom per molecule (3 for a monatomic gas) the average energy per molecule will be $\frac{3}{2}k_BT$, regardless of molecular mass. Equal increases in energy per molecule correspond to equal increases in energy, so both gases will have the same temperature increase.

Another way to look at this is in terms of heat capacities. For ideal gases, the molar heat capacity (heat added to a gas divided by temperature change) only depends on the number of degrees of freedom. In this case, the molar heat capacity (for the constant-volume gases) is $C_V = (3/2)R$, so the heat capacity for each gas is $(3/2)nR$. Adding the same amount of heat guarantees the same temperature increase.

So what does the molecular mass have to do with anything? The average kinetic energy per molecule for both gases will be the same, but the masses will be different and therefore the average speeds per molecule will be different for the two gases.

Mathematically,

$$\frac{1}{2}mv^2 = \frac{3}{2}k_BT \quad \rightarrow \quad v_{\text{rms}} = \sqrt{\frac{3k_BT}{m}}\,.$$

The speed above is known as the "root-mean-squared" (rms) average speed. It is the appropriate speed to consider how the molecules behave, on average. Clearly, the v_{rms} is inversely related to the mass. While the average energy per molecule will be the same, the more massive molecules will move slower than the less massive molecules.

Two gases in identical containers with fixed volumes have the same pressures and number of moles. One is monatomic, the other is diatomic. You add the same amount of heat to both. Which gets hotter?

1. the monatomic gas
2. the diatomic gas
3. both reach the same temperature
4. more information is needed

ANS: **1**—The monatomic gas gets hotter.

For the monatomic gas, the energy added is spread among the three translational degrees of freedom. For the diatomic gas, the energy added is spread among more degrees of freedom, including rotation in addition to translation. At room temperature, the heat capacity (at constant volume) for the monatomic gas is $nC_V = (3/2)nR$, while for the diatomic gas it is $nC_V = (5/2)nR$. Therefore, it requires more heat to achieve the same ΔT for a diatomic gas than for a monatomic gas.

Consider two identical containers with fixed volumes, each containing one mole of an ideal gas at a common temperature. One is a pure monatomic gas, the other is a pure diatomic gas. They are both immersed in a heat bath at a higher temperature. Which gas absorbs more heat?

1. the monatomic gas
2. the diatomic gas
3. they both absorb the same amount
4. more information is needed

ANS: **2**—The diatomic gas absorbs more heat.

A heat bath can be seen as a “reservoir” that can provide as much heat as necessary to change the temperature of each gas. As before, the diatomic gas will have the greater heat capacity. To get the same increase in temperature, you need to add more heat to the diatomic gas than to the monatomic gas.