MOLECULAR MOTIONS

VOL 17

SUMMARY:

Many properties of matter such as fluidity, vaporization and rates of chemical reactions indicate that molecular motion must be occurring and that the freedom of motion increases in going from the solid to the liquid to the gaseous state. The concepts of translational, rotational, and vibrational molecular motions allow the interpretation of the observed properties. The use of animation and dynamic models makes clear how the observed properties depend on the types of motion occurring at the molecular level.

PURPOSE:

To illustrate the types of motion present at the molecular level in solids, liquids, and gases, using mechanical models and animation.

OUTLINE:

1. *Space-filling models of crystals*
   Models and corresponding samples are shown for solid mercury, solid and liquid water, and dry ice. Observations of phenomena such as the melting of mercury, condensation of mercury vapor, and the sublimation of carbon dioxide indicate that molecules have motion that is not represented in the static models.

2. *Glass bead model*
   A good model of a monatomic molecular substance such as mercury is obtained by sandwiching a single layer of glass beads between two layers of glass. The model is vibrated to simulate the effect of temperature. The beads arrange themselves in the form of a close-packed crystal when the agitation is slow. When it is increased, the regularities disappear and the beads show increasingly random motions similar to those of molecules in liquids.

3. *Translational motion in gases*
   Heating liquid mercury in an evacuated tube causes condensation in the cooler portion of the tube. Performing the same experiment with the addition of chips of blue glass causes the blue glass to fly about violently. Apparently the translational energy of the mercury atoms drives the glass chips up into the tube. The action of the rapidly moving tiny gas molecules on the relatively huge pieces of glass is analogous to the Brownian motion phenomenon in the liquid phase.

4. *Animation shows translational, rotational, and vibrational motion in gases*
   Translational motion is motion from place to place. Rotation is a turning motion around the center of mass of a molecule, whereas vibration is a bond-bending or stretching motion within a molecule. Vibration is shown in formamide, water, and heavy water. Vibrational energy change in a diatomic molecule is shown in collision, and in the absorption and emission of light.

5. *Motion in a liquid*
   A mechanical model shows motion in a liquid. Since there is little open space, motion in a liquid consists mainly of hindered rotation with some net translation. A marked molecular model is placed in a shaking table of unmarked models and the obstruction to translational movement of a particular molecule in a liquid is depicted.

6. *Diffusion in liquids, gases, and solids*
   When aqueous permanganate solution is added to an aqueous iron (II) solution, the color change shows that reaction occurs as rapidly as the liquids mix. The ionic reaction is:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$$

colorless purple yellow colorless

   When the potassium permanganate is added in crystalline form, the crystal does not dissolve rapidly. Instead, there is a slow development of color near the crystal, defining a region in which iron (II) ion has been consumed. This colored region increases slowly, limited by the slow process by which the crystal dissolves and by the slow movement of the colored ions through the liquid. Stirring aids the molecular mixing, and more reaction occurs.

   When a vial of bromine is broken in a tall cylinder, diffusion in this case among gaseous molecules, is much more rapid. Diffusion is so slow in solids that it is usually difficult to observe.

7. *Effect of heat*
   A mixture of solid sulfur and zinc remains unreacted. A vigorous reaction occurs when the mixture is heated. Molecular motions increase as heat is added. When the rapidly moving molecules of liquid sulfur come into intimate contact with the zinc fragments, reaction is initiated. No reaction occurs between hydrogen and oxygen gases mixed at room temperature, but heat increases the energy of molecular collisions and reaction occurs.

SUPPLEMENTARY MATERIAL:

Different molecular motions become important at different temperatures. In gases at very low temperatures (50 K), translation is the only significant motion. At higher temperatures molecules of all but the monatomic gases also rotate. Vibration becomes appreciable for most molecules at higher temperatures, well above room temperature. In solids, vibrations of the atoms about their fixed locations in the lattice are important at all temperatures. Molecular rotation occurs in only the simplest molecular solids, such as solid hydrogen.

Questions To Ponder:

1. Discuss (a) translational, rotational, and vibrational motion, (b) the effect of temperature on molecular motion, (c) the nature of solid-liquid and liquid-gas phase changes in terms of molecular motion.

2. Why does rubbing two sticks together cause the sticks to become warm? (*Rubbing requires work on the two sticks against the force of friction. Since energy is conserved, this work appears as heat in the sticks. The warmth implies that molecular motions have increased.*)

3. Why is the ocean composed of freshwater near the mouth of the Amazon River even far out of sight of land? (*The rate of mixing of the freshwater and the ocean water is a relatively slow process because of the obstruction to molecular movement in a liquid. Since the river empties a large amount of freshwater into the sea, this freshwater moves far out to sea before mixing becomes significant.*)

4. The molar heat capacity is the amount of heat required to raise the temperature of one mole of a substance one degree Celsius.

Heat capacities of gases
(25°C, 1.0 atm. pressure) $Jmol^{-1}K^{-1}$

He	20.79
H_2	28.84
H_2O	33.58

Explain in terms of molecular motions why the heat capacity of gaseous helium is less than the heat capacity of gaseous hydrogen, which is, in turn, less than the heat capacity of gaseous water. (*For all gases, including helium, raising the temperature places more energy in the translational movements of the particles. For polyatomic molecules, raising the temperature also places more energy in the vibrational and rotational movements of the molecules. Hence hydrogen, H_2, has a higher heat capacity than monatomic helium. Water, with three atoms in non-linear arrangement, has more kinds of vibrational movement than hydrogen and three axes around which to rotate compared to two for hydrogen. Hence, gaseous water has a higher heat capacity than hydrogen gas.*)

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