H A&S 222d/253e Introduction to Energy and Environment: Life Under the Pale Sun
Spring 2007
Lecture 5.2 (07)

THERMAL ENERGY (2)

We described the specific heat capacity, which relates the heating of a substance to its temperature rise. Molecular vibrations and the kinetic energy of molecules flying around in a gas are responsible for this 'microscopic' energy we call 'heat'. Count Rumford's experiment attempted to measure the 'mechanical equivalent of heat' long before understanding of atoms and molecules had been achieved. Thus we could calculate the average speed of molecules of air around us simply by knowing how much its temperature rises for a given heat input (assuming the 'ideal gas' model which ignores molecular vibrations). Another insight into the nano-world of molecules comes from a simple lab experiment measuring the equation of state of air. Its pressure, P, volume, v, and temperature, T, are connected by $Pv = nR \cdot T$. If you use a glass syringe (see below) and flask to hold a volume of air, heating the flask as shown will expand the air at constant pressure (the air pressure of the lab is pushing on the movable part of the syringe, which moves to the left as air expands).

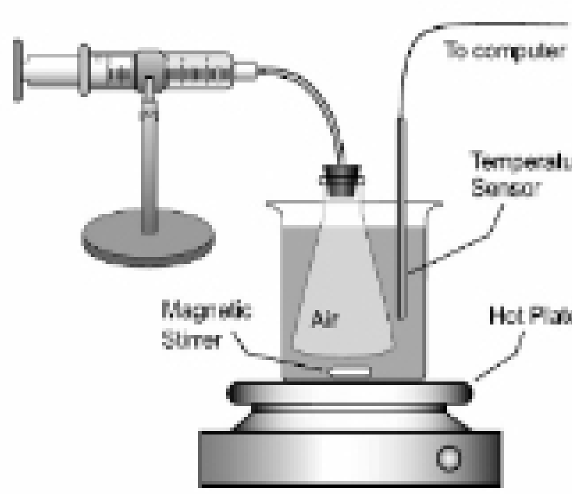


Fig. 5. Experimental setup for studying the temperature-volume relation of an ideal gas. An air-filled flask is submerged in a beaker of water that is heated with a hot plate. A flexible tube joins the flask to a glass syringe.

(Jackson, Am. J. Physics 2006)

The plot below (left) shows how the volume air varies with its temperature. Just as the equation says, it is a straight line. But the remarkable thing is that you can extrapolate the line to the left to where the air would occupy infinitesimal volume. This gives us a measurement (or prediction) of the temperature we call *absolute zero*. In this particular experiment the number came out to be -267°C, which is quite close to the accepted value, -273.15°C or 0K. Close to absolute zero molecules slow down and many curious properties appear, like superconductivity (electrical conductivity with no ohmic resistance) and superfluid property that the viscosity vanishes…the fluid has no friction forces. These properties make possible remarkable, practical devices like super-magnets, mag-lev trains, frictionless fluid flow and quantized vortex motion. The righthand curve below is simple Pv=constant relation for isothermal ..constant temperature… compression of air.

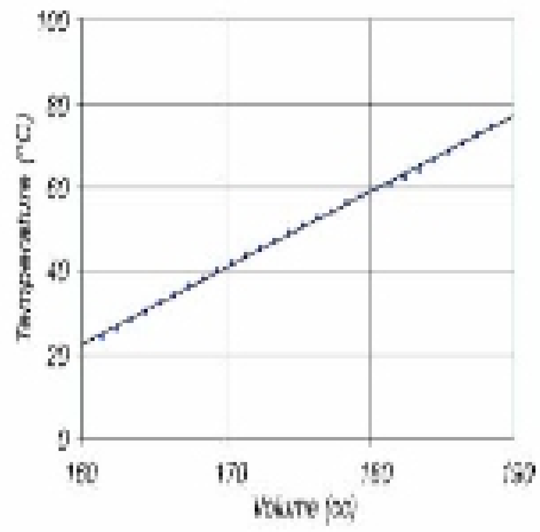


Fig. 6. T-V data obtained using a 30-ml glass syringe. A least-squares linear fit also is shown. Extrapolating to zero volume gives an absolute zero of −267 °C.

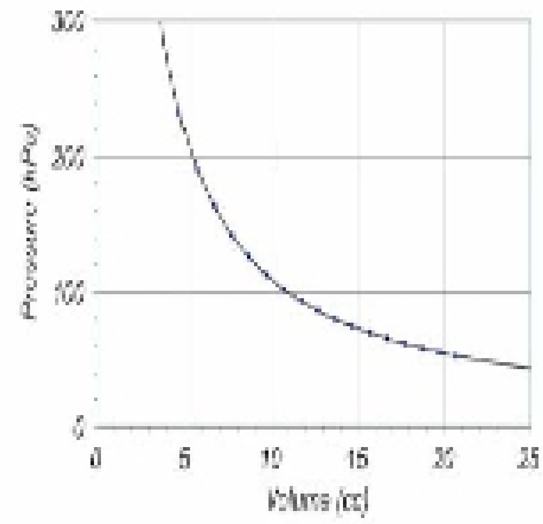


Fig. 8. P-V data obtained using a 20-cc plastic syringe. The curve is a least-squares fit of the form $P=c/V$, where c is a constant.

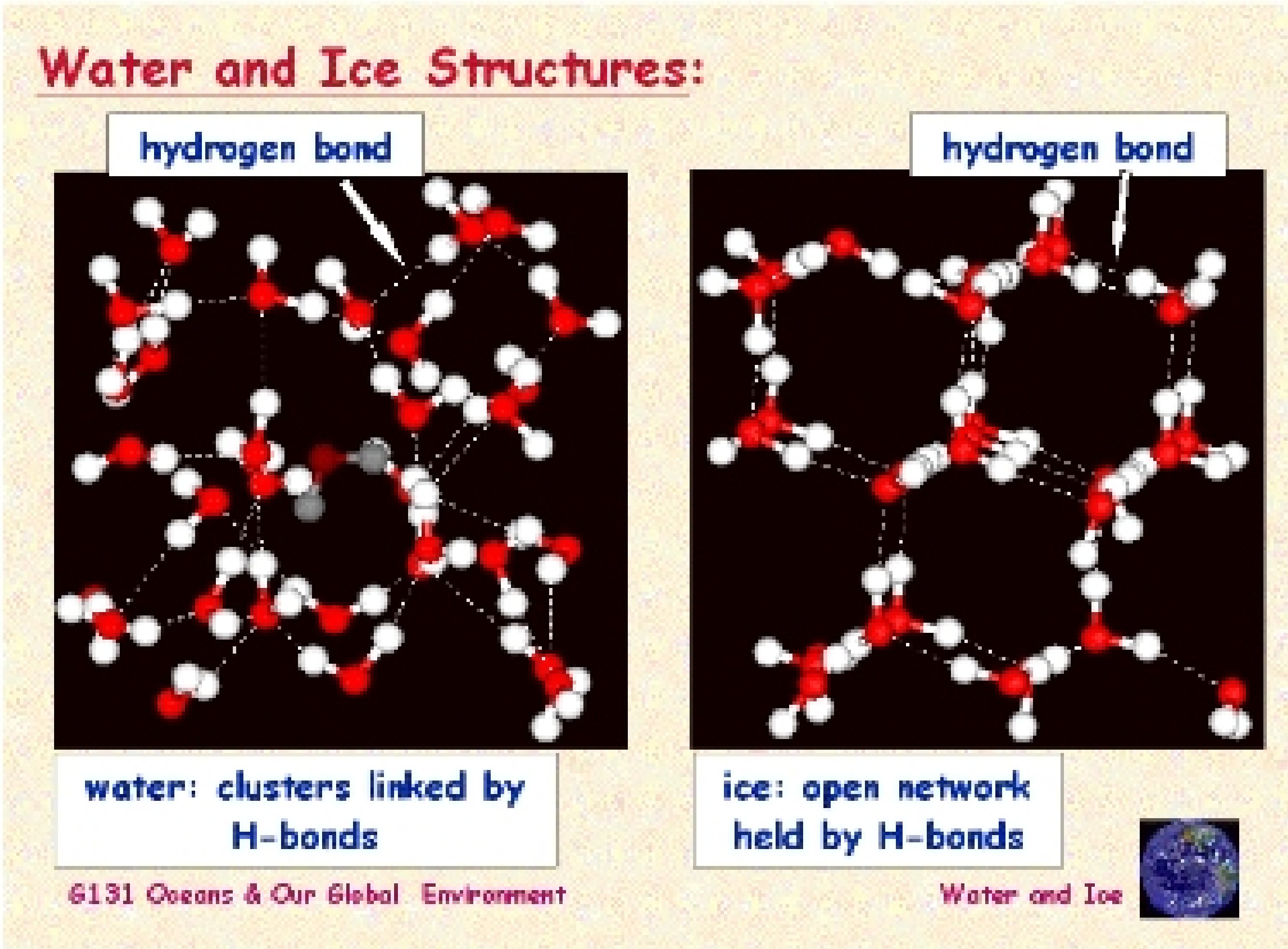
PHASE CHANGE ('CHANGE OF STATE')

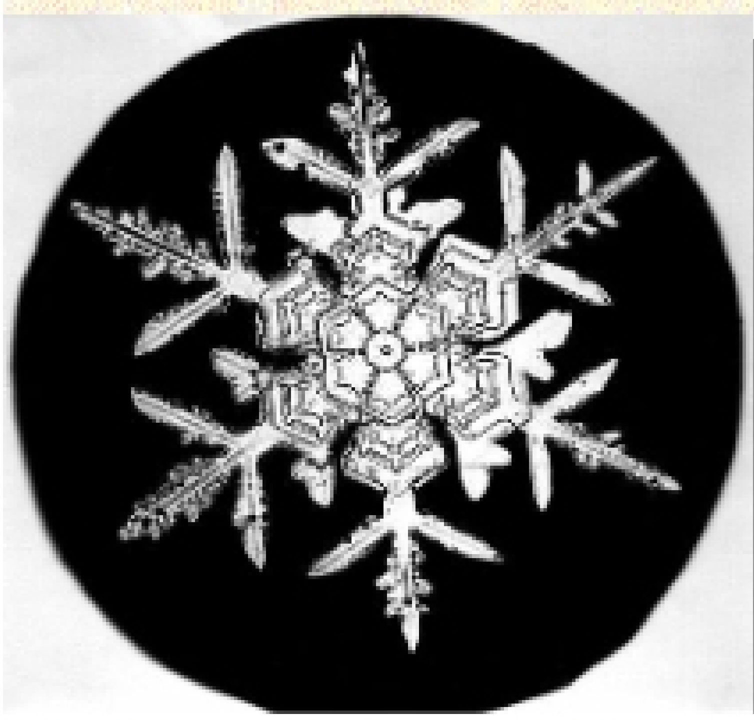
A substance like water can exist in solid, liquid or gaseous form. Intermolecular forces, particularly the hydrogen bonds related to the molecule H_2O, hold molecules in a rigid crystal lattice when it is solid ice. The shape of the molecule favors a six-sided crystal, which dictates the symmetry found in snowflakes (the microscopic shapes combine to make the visible crystal). This symmetry comes from the shape of the water molecule, as we see in the next paragraph.

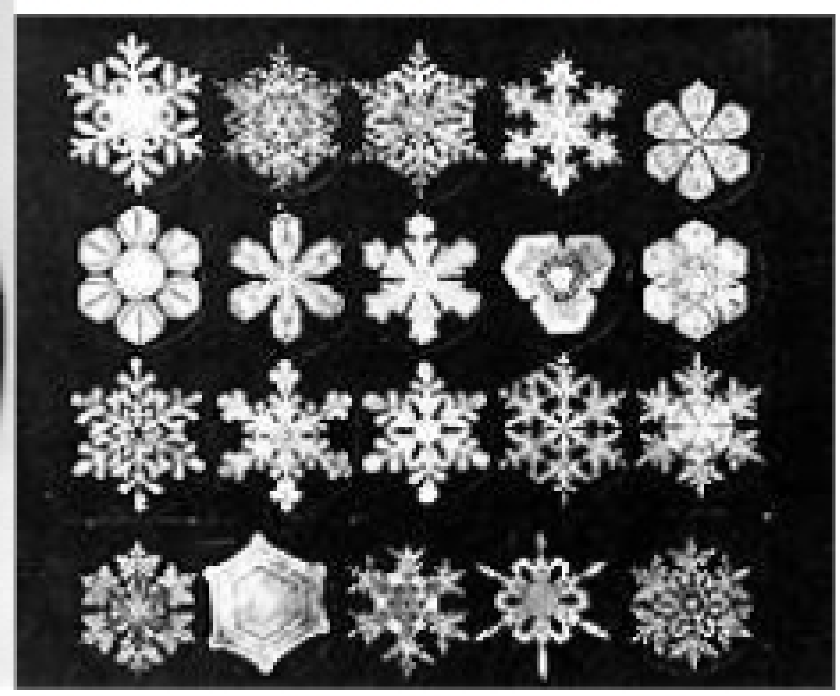
Hydrogen is the simplest atom of all…a positively charged proton with a negatively charged electron orbiting around it like the moon around the Earth. The water molecule has its 2 hydrogen atoms connected to its 1 oxygen atom with a 'dog-leg' angle of 104.5^0. The size of each leg of the water molecule is about 0.2×10^{-9} m which is smaller than the size of a hydrogen atom by itself (the diameter of the electron orbit is about 0.5×10^{-9} m). The electronegativity of oxygen is extremely high…it is an electron eater…and so the one electron orbiting each hydrogen atom is pulled toward the oxygen atom, leaving the hydrogen atoms as 'naked protons' at each end of the molecule. This means that water is a 'polar' molecule, with its ends positively charged and its center negatively charged. Two water molecules are attracted to one another by these charges (sort of nose-to-tail…the ends of one molecule being attracted to the center of another). Water is very unusual, and a key substance for life on Earth. This polar property is one reason. The hydrogen bonds between water molecules are about 1 to 2 KJ/mol which is fully 5% as strong as a typical covalent bond within a single molecule…this is pretty strong. Strong inter-molecular forces mean that molecules of solid water (ice) are hard to pull apart…the melting point of ice is higher than for other substances of similar molecular weight. Likewise the liquid is hard to pull apart to make gaseous water…water vapor. Thus the boiling point of water is higher than expected for similar compounds. The figure below shows oxygen (red) and hydrogen (white) atoms in liquid water (left) and ice (right). The 104.5^0 angle is visible, in each molecule. and the attraction between molecules….the hydrogen bond…is apparent in the way they sit relative to one another.

We come to think of phase change

The hexagonal (6 sided) shape of the ice structure and 6-fold symmetry of snowflakes comes from the 104.5^0 angle of the H_2O molecule…which is close enough to the 120^0 angles inside a hexgon.







Under the microscope, I found that snowflakes were miracles of beauty; and it seemed a shame that this beauty should not be seen and appreciated by others. Every crystal was a masterpiece of design and no one design was ever repeated., When a snowflake melted, that design was forever lost. Just that much beauty was gone, without leaving any record behind."

Wilson "Snowflake" Bentley 1925

When heated, molecular vibrations loosen these bonds and the liquid state still involves hydrogen bonds, but without rigid order. Further heating breaks the molecules far apart, into a gas with large separation between molecules. Each transition, melting or boiling, requires an input of thermal energy to break the bonds (that is the potential energy stored in the bond forces). When we heat ice its temperature increases steadily until it starts to melt, at which time most or all of the heating goes