Classroom Photocopying Permission

Experiments from Teaching General Chemistry: A Materials Science Companion. Copyright © 1993 American Chemical Society. All Rights Reserved. Multiple copies of the experiments may be made for classroom use only, provided that the following credit line is retained on each copy: "Reproduced with permission from *Teaching General Chemistry: A Materials Science Companion*." You may edit the experiments for your particular school or class and make photocopies of the edited experiments, provided that you use the following credit line: "Adapted with permission from *Teaching General Chemistry: A Materials Science Companion.*"

Overhead Masters
Multiple copies of the overhead masters may be made for classroom use only, provided that the extant credit lines are retained on each copy: "© 1993 American Chemical Society. Reproduced with permission from *Teaching General Chemistry: A Materials Science Companion*" or "© 1995 by the Division of Chemical Education, Inc., American Chemical Society. Reproduced with permission from *Solid-State Resources* ."

Laboratory Safety

DISCLAIMER

Safety information is included in each chapter of the Companion as a precaution to the readers. Although the materials, safety information, and procedures contained in this book are believed to be reliable, they should serve only as a starting point for laboratory practices. They do not purport to specify minimal legal standards or to represent the policy of the American Chemical Society. No warranty, guarantee, or representation is made by the American Chemical Society, the authors, or the editors as to the accuracy or specificity of the information contained herein, and the American Chemical Society, the authors, and the editors assume no responsibility in connection therewith. The added safety information is intended to provide basic guidelines for safe practices. Therefore, it cannot be assumed that necessary warnings or additional information and measures may not be required. Users of this book and the procedures contained herein should consult the primary literature and other sources of safe laboratory practices for more exhaustive information. See page xxv in the Text 0 Preface file in the Companion Text folder for more information.

Chapter 2

Atoms and Electrons

The story line in chemistry is atoms, the building blocks of matter, and their electrons. The sharing and transferring of electrons permits atoms to combine with one another in chemical reactions that lead to new forms of matter. Until recently, we had only indirect evidence for the existence of atoms, obtained by such methods as stoichiometric relationships, spectroscopy, diffraction methods, and thermodynamics. As noted in Chapter 1, however, it is now possible to directly image atoms on the surface of a material. This chapter illustrates the use of solids to provide direct and indirect evidence for atoms.

Direct Evidence for Atoms: The Scanning Tunneling Microscope

Progress in the development of analytical instrumentation has enabled scientists to characterize and manipulate matter with ever-greater spatial resolution. Nowhere is this more evident than in the development of the scanning tunneling microscope (STM). Developed in the mid-1980s, the STM permits direct imaging of atoms. An STM specifically designed for undergraduate laboratory and classroom use has recently been marketed,[1] and a paper describing a student experiment and containing references to a number of applications of scanning tunneling microscopy has been published *(1)*.

To put the STM experiment in context, consider the simple circuit shown in Figure 2.1. When the circuit is complete, the light bulb will light:

---

[1] The Burleigh instructional STM (*see* Supplier Information)

2725-X/93/0015$09.50/1

electrons are pumped through the circuit as the battery's chemical energy is converted to electricity. If the wire is cut, however, and the cut ends are not in contact, the light is extinguished, because there is no longer a complete circuit for the electrons. If the wire ends are brought into contact, the bulb can again glow. This experiment raises an interesting question: How close must the two ends of the cut wire be for electrical current to flow? The question is difficult to address experimentally because of the unimaginably large numbers of Cu atoms on the two surfaces of the wire ends. Each surface is probably quite rough on the atomic scale, and thus the atoms of the two surfaces are collectively at a variety of distances from one another.

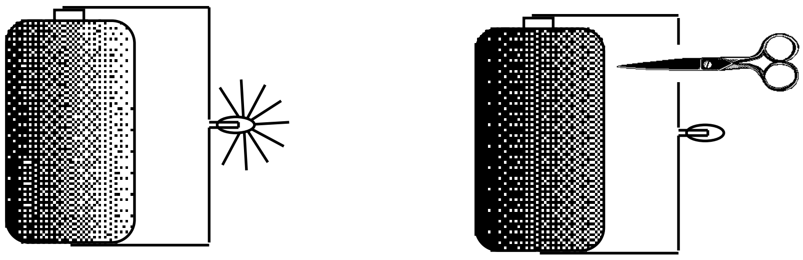

Figure 2.1. A simple electrical circuit containing a battery and a light bulb. When the connecting wire is cut, the circuit is open and the bulb will not light.

Now, however, imagine that one of the wire ends can be sharpened to a tip of one-atom dimension, an “atomic tip”, and brought close enough to the surface that current can again flow, as shown in Figure 2.2. Furthermore, imagine that this tip can be moved in atomic-scale increments laterally across the surface. As it moves, it samples the atomic surface topography through variations in current as the tip-to-surface height varies (Figure 2.3). Alternatively, the tip-to-surface height can be continuously adjusted with atomic-scale resolution so that a constant current flows while the tip moves along the surface. By either method, the spatial arrangement of atoms on the surface is determined by the variation in electron density sensed by the probe tip as it traverses the surface. This is, in fact, how the STM operates.

How close does the tip need to be to the surface? Only within a few angstroms (10^{-8} cm) because of a quantum mechanical phenomenon called tunneling. An easy way to look at tunneling is to begin by considering one atom. The electrons surrounding the atomic nucleus are not confined to a hard shell but rather have a smoothly varying distribution, meaning that the edge of an atom is indistinct. If the quantum mechanical equations describing the probability of finding an electron at a given distance *r* from the nucleus at any time are solved, the probability distribution of the electron, *P(r)*, would look something like

$$P(r) = A\, e^{-r/r_o} \qquad (1)$$

where *A* is a constant and r_o is the Bohr radius. From this equation it can be shown that the electron spends most of its time near the nucleus and less time at larger, but unbounded, distances. This probability distribution falls off rapidly—exponentially—with distance from the nucleus.

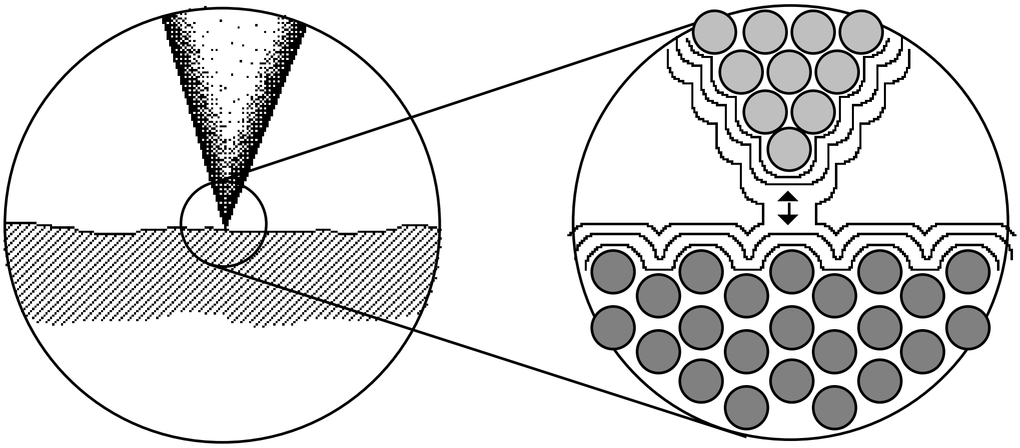

Figure 2.2. A sketch of an atomically sharp tip near a surface.

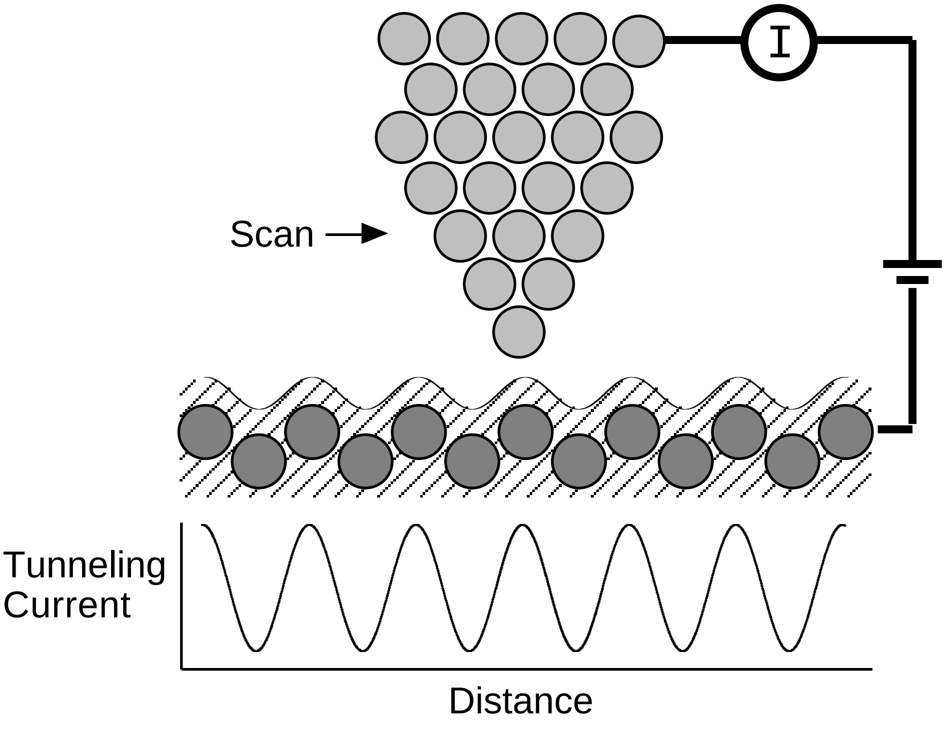

Figure 2.3. A plot of tunneling current as a function of horizontal probe tip position. The absolute vertical position is held constant. When the tip is nearest the surface atoms, the current is highest. The wavy line above the shaded circles represents the contour of the surface.

Now consider two atoms A and B that are within angstroms of one another, with their associated electron probability distributions, *P(r)*, as sketched in Figure 2.4. An electron initially on atom A can move through the region of overlapping electron density to become part of atom B's electron cloud. This movement of the electron is forbidden by classical physics, because the electron does not have sufficient energy to make the transfer between atoms; however, electrons actually behave as described by quantum mechanics and have a non-zero probability for the process. The motion of the electron through a classical barrier is called tunneling. Thus, an electron may tunnel from an atom in the probe tip to an atom on the surface (or vice versa).

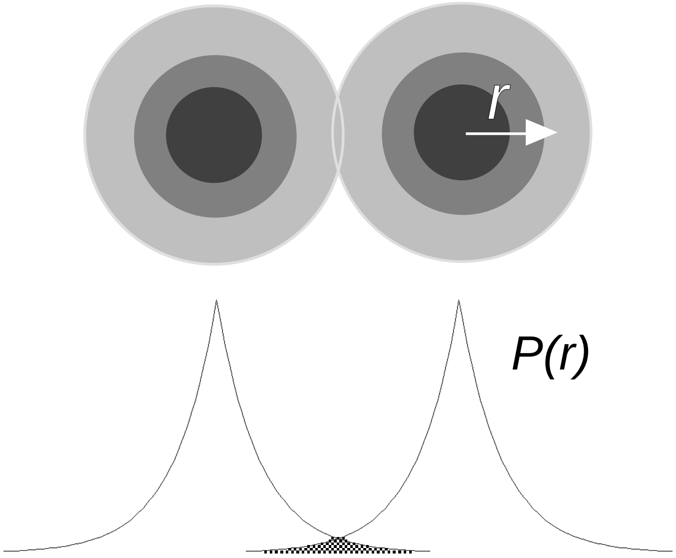

Figure 2.4. Two atoms with their electron probability clouds slightly overlapping. In the top part of the figure, the atoms are represented as spheres with overlapping volumes. In the bottom part of the figure, the graphical representations of the electron probabilities (as a function of distance from the nucleus) are seen to overlap.

The use of an applied potential in an STM experiment leads to a continuous current, because atoms A and B are part of conducting materials like metals or semiconductors (electrical conductivity is discussed in Chapter 7). The electron probability distributions fall off exponentially with distance; therefore, the tunneling current provides a very sensitive probe of interatomic separation.

As the tip moves across the surface at a constant height, the tunneling current will change because the overlap between the tip atom and the surface atoms will change. When the tip is directly over a surface atom, the tunneling current will be higher than when the tip is between two atoms. Higher currents mean that the substrate being investigated has a higher surface height and a shorter tunneling distance.

A problem with studying the surface in this manner is that because the tip is only a few angstroms from the surface, it is easy to crash it into the sample unless the substrate is smooth on the atomic scale. To circumvent this problem, the STM is usually operated in constant-current mode, which makes use of a feedback controller. The feedback controller measures the actual tunneling current and compares it to a desired value that the operator can control. (For an example of a feedback controller from physiology, consider trying to balance a yardstick positioned vertically in the palm of your hand. It is much easier to do when your eyes are open—the eye provides feedback that allows the hand to move to compensate for the shifting of the yardstick.)

The tip is connected to a positioner that is in turn connected to the feedback controller. Voltages from the feedback controller change the length of the positioner so as to pull the tip away from the surface if the current is higher than desired, or to lower the tip toward the surface if the current is lower than desired. In this way, the desired current value is maintained as the tip scans above the surface. The change in the positioner's length is directly proportional to the applied voltage, so that the changes in voltage produced by the feedback controller are directly proportional to the changes in surface height.

A computer is used to control the location of the STM tip, and at each location on the surface, the computer measures the surface height based on the voltage applied to maintain constant tunneling current. This two-dimensional array of numbers, representing heights at different positions in the area surveyed, is often displayed through gray-scale imaging: high locations are represented as white, and low locations as black, giving a picture that is essentially what a photograph of the surface would look like. An image of a surface of silver atoms is shown in Figure 2.5. The silver atoms on this surface are close-packed (Chapter 5). The STM does not really give the physical positions of the atoms, but senses their electrons and bonds. As a result, the current detected depends on both the tip-to-atom distance and the chemical identity of the surface atoms.

How is an STM tip prepared so it terminates in a single atom and how does the positioner work to permit control of the tip's position on the atomic scale? The tips are usually either made of W or Pt. For STM studies in vacuum environments, W is usually preferred because of the relative ease in preparing a single-atom-terminated tip. If the STM is to be operated in air or liquid, the ease with which W oxidizes precludes its use, and Pt or Pt–Ir alloys are preferred, although tips from these materials are more difficult to prepare and generally are not as atomically sharp.

Tips are usually made by an electrochemical etching process, starting with fine wire. With W, the wire is held vertically and partially immersed in an aqueous solution of base. When a 5-V potential is applied to the wire, the W surface is oxidized to a dense, soluble oxide. The tungsten oxide flows down past the tip and prevents further electrolysis except where the wire enters the solution. For Pt and Pt–Ir alloys, an alternating current etching procedure is employed. In either case, localized etching results in a “neck” in the wire. Eventually, the wire will be etched through at this thinnest part, and the bottom part falls off. The tip often terminates in a small cluster of atoms or the desired single atom.

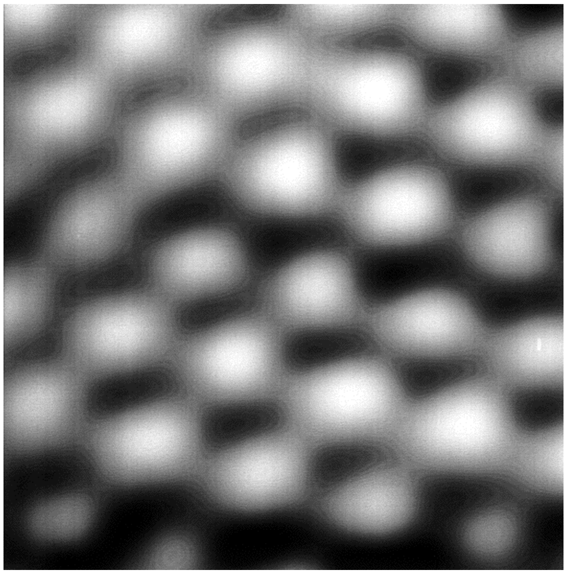

Figure 2.5. The STM image of a close-packed layer of Ag atoms. (Photograph courtesy of Robert Hamers.)

The tip's position is controlled with a piezoelectric scanner. Piezoelectric materials are ceramic materials that will expand or contract when a voltage is applied to them (conversely, mechanical deformation can yield a voltage; *see* Chapter 1 and a later section of this chapter for further discussions of piezoelectricity). The most common way of using piezoelectric materials for tip positioning is to take a single tube of piezoelectric material and to place four metal electrodes on the outside of the tube and a single electrode on the inside (Figure 2.6). Appropriate combinations of voltages applied to these electrodes can make the tube extend or contract along its length and/or bend in any direction. The tip is mounted on the axis of the tube, at its end. When the tube expands or contracts, the surface-to-tip separation decreases or increases, respectively. When the tube is made to bend, the amount by which it bends is small compared to its length, so that the tip moves mainly sideways. A typical piezoelectric scanner requires voltages on the order of 100 V, and the tip can move inside a square scan area with 4-μm (0.004-mm) sides. Because the tunneling current can be detected only when the sample and tip are less than about 10 Å apart and the positioner can only move a few micrometers, levers, gears or other piezoelectric translators are used to bring the tip to within a few micrometers of the sample without crashing the tip into it. In designing an STM instrumental setup, the apparatus must be isolated from room vibrations and temperature fluctuations, which can cause crashing and smear data.

In principle the STM can be applied to a variety of problems spanning the spectrum of science and engineering. In practice, many studies have focused on the properties of “clean” surfaces or surfaces that have been modified in some controlled way. Even at a pressure of 10^{-6} torr (10^{-4} Pa), each atom on a surface will undergo one collision with a gas-phase molecule per second, and a surface will likely react or become contaminated in about a second. Pressures of 10^{-10} torr (10^{-8} Pa) are needed to study surfaces for periods of hours without contamination. STMs that are compatible with such high-vacuum conditions require special materials.

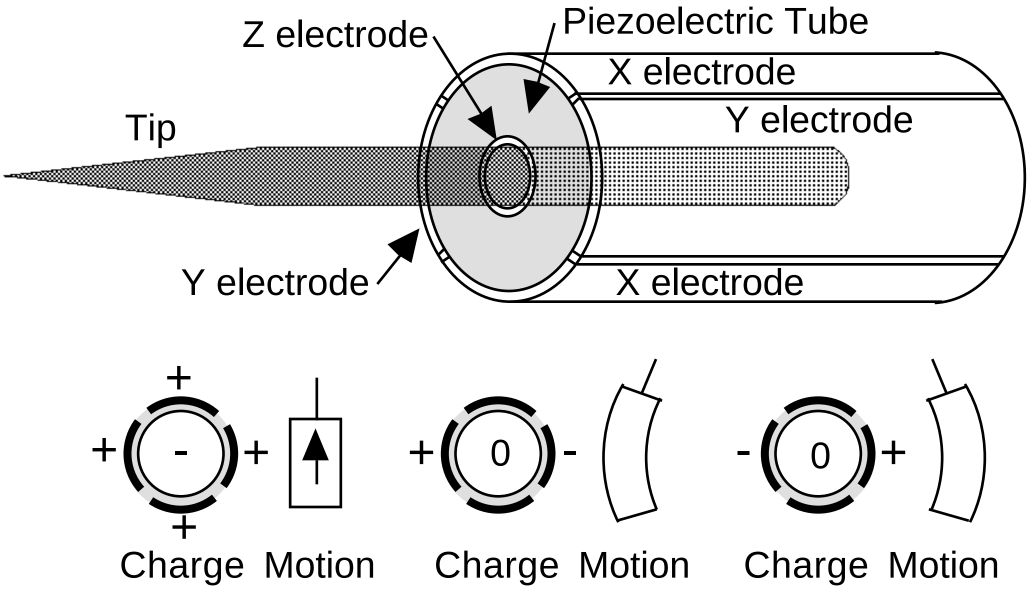

Figure 2.6. A piezoelectric tube. Top: Enlarged view. Bottom: The effect of various applied voltages on the position of the tip. (Adapted with permission from reference 2.)

The STM can also be used to study electrode surfaces immersed in liquid electrolytes. In this case, there can be faradaic currents resulting from solution electrochemical reactions in addition to tunneling currents. To image the electrode surface ideally requires insulating the tip except for the atoms at the tip end (Figure 2.7). In practice, if the total exposed tip is smaller than about 1 μm, typical electrolyte concentrations and applied voltages produce faradaic currents that can be neglected compared to the tunneling current.

The application of STM to biological molecules has been of interest and even proposed as a method for gene sequencing. For any molecule to be observed with the STM, however, it must be attached to a rigid, flat, conductive material. Thus, the molecule–substrate interaction must be strong enough to anchor the molecule so that it can be imaged, but not so strong that the molecule is altered by the anchoring. Large molecules have been imaged either by depositing them onto flat substrates like graphite or gold and then doing the STM experiment in vacuum; or they can be adsorbed in electrolyte solutions and the STM experiment performed in situ. Finding substrates that will hold biological molecules rigidly without tearing them apart has been a problem; some early images claimed to be DNA were later shown to be features in the graphite surfaces. The STM being marketed for educational use can be used to image a long-chain hydrocarbon ($C_{32}H_{66}$) that orients itself on a graphite substrate.

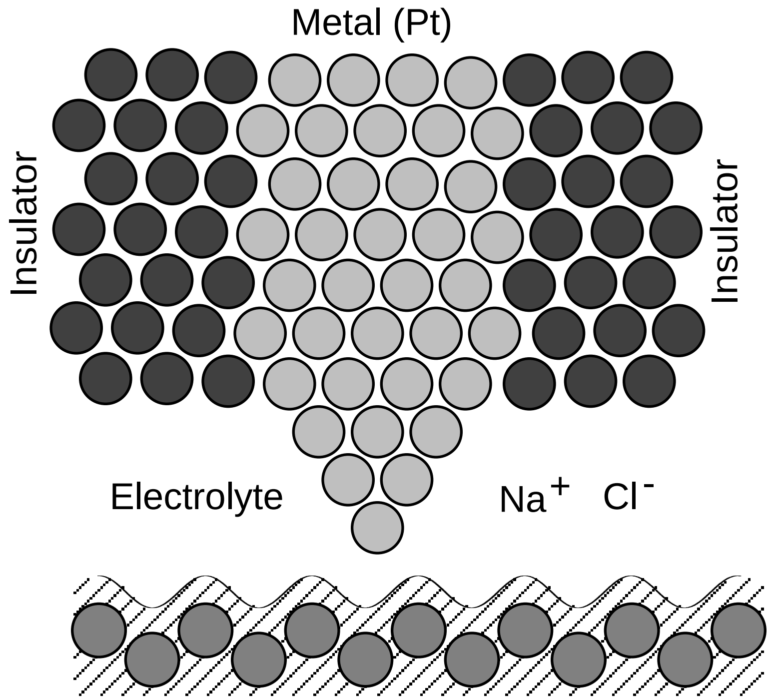

Figure 2.7. An insulated atomic tip can be used to probe electrode surfaces. The wavy line above the shaded circles represents the contour of the surface.

As noted in Chapter 1, the STM can even be used to position atoms. Researchers at IBM were able to manipulate xenon atoms on a metal surface to spell out “IBM.” This was done by cooling a single crystal of nickel metal to 4 K under high vacuum and condensing some Xe atoms onto the surface. The Xe atoms were initially at random locations and were detected with the techniques described earlier.

To move an atom, the tip was placed above the atom and lowered to a closer distance than is normally used for scanning. The tip was then moved across the surface at a speed of 4 Å per second, dragging along the xenon atom. Most likely, the main interaction between the tip and the xenon atom is due to van der Waals forces *(3)*.

These same techniques may be used to fabricate atomic-scale devices and new structures. In fact, the STM has been used to prepare a “nanobattery.” The battery (Figure 2.8) consists of two copper pillars and two silver pillars that are deposited sequentially on a graphite surface by electrochemical reduction of solutions of copper sulfate and silver fluoride. An STM tip serves as an electrode that is fine enough to deposit these very small pillars. This nanometer-scale galvanic cell (about the size of a common cold virus) is estimated to generate about 0.020 V.

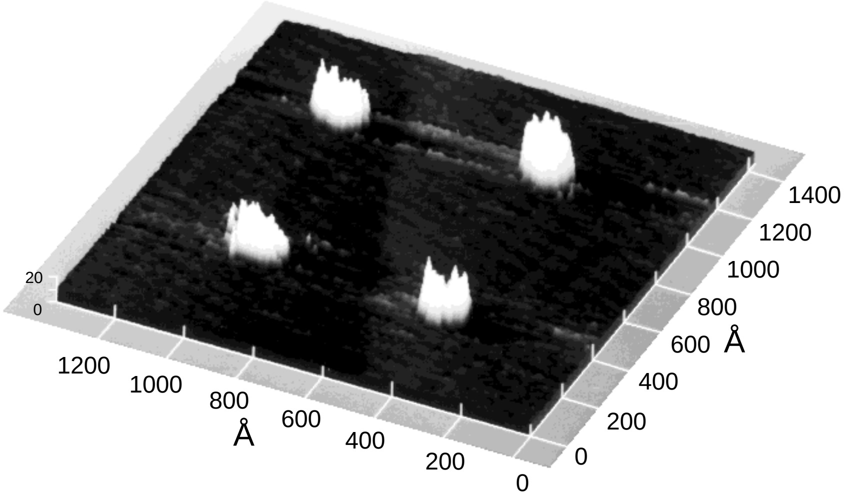

Figure 2.8. STM images of a copper–silver nanometer-scale cell on graphite. The two structures on the right are electrochemically deposited silver, and the two structures on the left are electrochemically deposited copper. In a copper solution the cell is galvanic; the copper pillars decrease in size and copper metal plates onto the silver pillars. (Reproduced from reference 4. Copyright 1992 American Chemical Society.)

A close relative of the STM that is being applied to many of the same experimental systems is the atomic force microscope (AFM). The AFM operates by sensing the force between surface atoms and the atom in a tip rather than by measuring the current. Thus, the AFM can be used to study electrically insulating materials. To measure interatomic force, the tip of the AFM is mounted on the end of a small lever. As the interatomic force varies, the deflection of the lever can be sensed by bouncing a laser beam off the back of the lever and measuring displacements with a pair of photosensors.

The STM can be operated in air. Stable surfaces are provided by a variety of materials, including layered solids like graphite and molybdenum disulfide. The layered nature of these solids and the weak van der Waals forces holding the layers together permits layers to be removed easily to create fresh surfaces (Chapter 5 gives more information on graphite and molybdenum disulfide).

Indirect Evidence for Atoms: Heat Capacities

Given the tremendous diversity in elemental solids and their properties, it is surprising to find that many of them share a common feature: At sufficiently high temperatures (often room temperature is adequate) many of the elements, particularly the metallic elements, have approximately the same molar heat capacity of ~25 J/mol-deg. Heat capacity must be more strongly related to the number of atoms of matter present than to the mass of matter. This finding, often called the law of Dulong and Petit *(5)*, served as the basis for an important empirical method of estimating atomic masses in the 1820s. Moreover, the molar heat capacity relationship can be extended to many ionic solids, because the total number of particles in the solid, either atoms or ions, determines the heat capacity.

To understand the experiment and its implications regarding atoms, consider first a collection of gaseous atoms. The average kinetic energy of a mole of a monoatomic gas is 3/2 RT, where R is the gas constant and T is the absolute temperature in kelvins. This fact illustrates the equipartition theorem: At thermal equilibrium, there is on average 1/2 RT of energy for each independent degree of freedom in a chemical system; because the gas atoms can move freely in three mutually perpendicular dimensions (x, y, and z), their average energy is 3/2 RT. A temperature change of a degree thus corresponds to a molar change in heat content or molar heat capacity for the gas of 3/2 R or ~12.5 J/mol-deg. For polyatomic gas molecules, additional contributions to the heat capacity can come from rotational and vibrational motion *(6)*.

Now consider a crystal of metal atoms in which each atom is connected to its neighbors through a network of imaginary springs. For most metallic elements, room temperature provides sufficient thermal energy to cause all the atoms to vibrate as they absorb the ambient thermal energy. The total energy of these vibrating atoms comprises both kinetic and potential energy contributions that are continuously interconverting. According to the equipartition theorem, the six degrees of freedom (three for the three dimensions of motion associated with kinetic energy and three for the three dimensions associated with potential energy) lead to an average thermal energy of $6 \times 1/2\ RT = 3RT$, and thus a molar heat capacity of $3R$, ~25 J/mol-deg.

The molar heat capacity value of 25 J/mol-deg is a high-temperature limit that can be achieved only if all the normal vibrational modes of the solid can be excited. For several of the lighter elements like Be and C (diamond), the vibrational frequencies are relatively high; thus, temperatures substantially above room temperature are needed to activate these modes and reach the limiting heat capacity. (The frequency of a simple harmonic oscillator varies as $1/\sqrt{m}$ where m is the mass, and room temperature does not supply enough ambient thermal energy to activate all of the vibrational modes.)

Figure 2.9 illustrates the temperature dependence of the molar heat capacities for diamond, aluminum, lead, and copper. Aluminum, lead, and copper are typical metallic elements that reach the high-temperature limit by room temperature. As temperature is reduced, atomic vibrations and their contribution to heat capacity are no longer activated. At very low temperatures, the much smaller heat capacity due to freely mobile electrons in metallic solids (Chapter 7) begins to be the dominant contributor to the measured heat capacity.

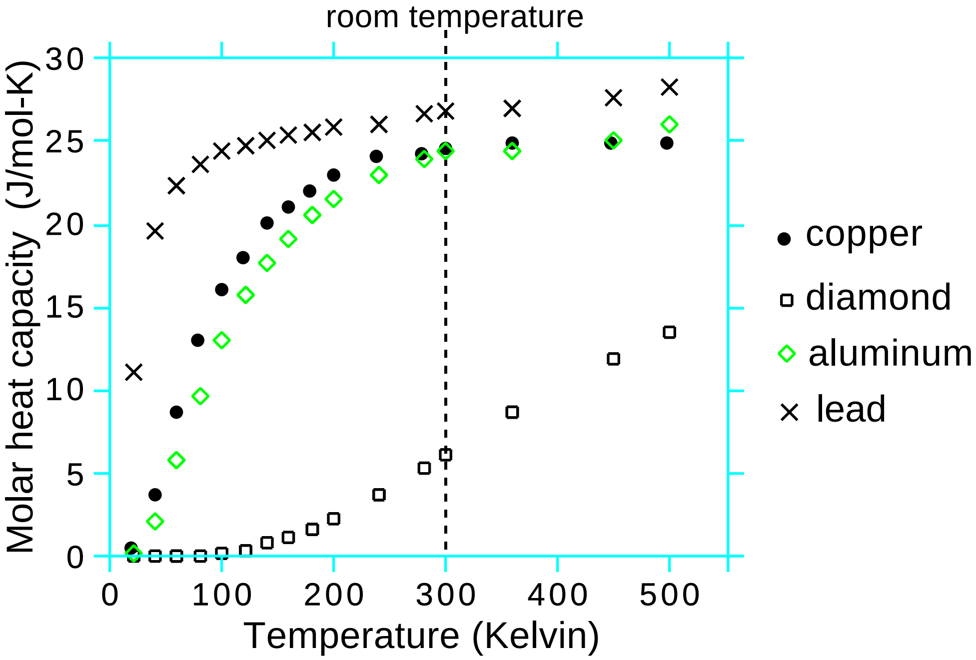

Figure 2.9. Plot of molar heat capacity versus temperature for copper, aluminum, lead, and diamond. (Data taken from references 7 and 8.)

Monatomic solids have heat capacities of $3R$. Based on the preceding discussion, we predict that polyatomic solids like salts would have a high-temperature heat capacity limit of $3R \times p$, where p is the number of atoms in the chemical formula of the solid. Thus, salts like NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, MgO, and CaO are all predicted to have a molar heat capacity of $3R \times 2 = 6R$ (~50 J/mol-deg), because there are two atoms per formula unit; likewise, CaF_2 and SiO_2 are predicted to give values of $3R \times 3 = 9R$ (~75 J/mol-deg); and $BaSO_4$ is expected to have a molar heat capacity of $3R \times 6 = 18R$ (150 J/mol-deg). All of these solids have measured molar heat capacities that are, at room temperature, good to better than within ~85% of the predicted values (Table 2.1).

Table 2.1. Molar Heat Capacities of Selected Solids at 298 K

Solid	Experimental Value	Theoretical Value
Al	24	25
Sb	25	
Be	16	
B	11	
Ga	26	
Mg	25	
Pb	26	
Te	26	
NaF	47	50
NaCl	55	
NaBr	52	
NaI	54	
MgO	44	
CaO	53	
CaF_2	66	75
SiO_2	73	
Na_2O	69	
$SrBr_2$	75	
KIO_3	106	125
$BaSO_4$	128	150
K_2SO_4	131	175

NOTE: All values are given in joules per mole-kelvin.
SOURCE: Adapted from reference 9.

Demonstration 2.1 shows that Al and Pb have greatly disparate gram specific heats (J/g-°C, the number of joules of heat needed to raise the temperature of 1 g of the substance by 1 °C) but common molar heat capacities (J/mol-°C, the number of joules of heat needed to raise the temperature of 1 mole by 1 °C).

Demonstration 2.1. Specific Heat and Molar Heat Capacity

Materials

- Aluminum and lead blocks with equal masses (masses in the range of 100 g to 1 kg work well) or equal moles (optional). *See* Supplier Information.
- Double-pan balance (or digital balance)
- Large beaker (must simultaneously contain both metal blocks)
- Hot plate
- Tongs or string
- Thermometer (ideally a digital thermometer, or one that can be read by the entire class)
- Two smaller beakers (to contain Al and Pb blocks separately)
- Water

Two glass rods

Procedure

- Place the metal blocks on a double-pan balance to show that they have equal masses. Alternatively, weigh them separately and compare the masses to show that they are the same.
- Place the metal blocks in a large beaker of boiling water. Make sure that there is enough water to completely cover the blocks. Maintain this temperature for several minutes to ensure complete heating. Measure the temperature of the boiling water.
- Place equal amounts of water at room temperature in the smaller beakers. Choose the beaker and water volumes so that placement of the metal blocks in the beakers will not cause the water to overflow. Measure the temperature of the water.
- Using the tongs (or, alternatively, a string that has been tied to each object), quickly transfer the metals, one to each of the smaller beakers of water.
- Stir the water with the glass rods. Measure the temperature of the water in each beaker, recording the highest temperature reached. The bath containing the aluminum will reach a higher temperature than the bath containing the lead (the same mass of Al has about eight times as many atoms, based on the relative atomic weights of the two elements).

Variations

- Knowing the actual masses of the metals, the volume of water used in the smaller beakers, the temperature of the boiling water bath, and initial temperature and the highest temperature reached by the baths containing the metals, the gram specific heats and molar heat capacities for each metal can be calculated to a reasonable level of accuracy, as described in most introductory chemistry texts. If the mass of water into which the metal is immersed equals the mass of the metal, the calculation of specific heat is simplified, as described in Experiment 1.
- The same demonstration can be performed with blocks of metal that contain the same number of atoms. This will produce the same temperature change in equal amounts of water.

Laboratory. A laboratory experiment that permits a class to pool its data for a variety of metal elements to discover these heat capacity relationships is described in Experiment 1.

Electrons in Solids

Just as the scanning tunneling microscope and the measurement of heat capacity provide evidence for the existence of atoms, the magnetic and electrical properties of solids provide evidence for the existence of electrons. Electrons may exhibit localized behavior, meaning that they are associated with one particular atom, bond, or ion. Electrons can also exhibit delocalized behavior, being shared among several atoms as in benzene or among larger numbers of atoms as in an entire crystal. The electromagnetic properties of a solid reflect not only the bonding character of its electrons, but their spin and charge, as well.

Electrons have two spin states, corresponding to the m_s quantum numbers +1/2 and –1/2, spin up and spin down. A single electron, e.g., spin up, without a corresponding spin down electron, is called an unpaired electron and in both molecules and solids can produce magnetic effects that, as shown later, can be used to augment traditional presentations of electronic configurations and formal oxidation states in introductory chemistry courses. The rich diversity of magnetic properties arising from unpaired electrons can also be demonstrated with paramagnetic and ferromagnetic materials.

Because electrons are mobile electrically charged particles, they are easily displaced in a solid by applied electric fields or by mechanical deformation. This can give rise to interesting electrical effects, the simplest of which is electrical conductivity. Described in this chapter is an electrorheological fluid which, as discussed in Chapter 1, is an example of a “smart” material; and common devices based on piezoelectric solids, which are the crystals used in watches and as strikers for lighters. These materials, whose use depends on induced electric dipoles in the solids, can be used to complement traditional discussions of molecular dipole moments in introductory courses.

Paramagnetism

In the majority of molecules and solids, all of the electrons are paired, and the molecule or solid is said to be diamagnetic. Several types of magnetic behavior are possible, but the largest magnetic effects result from the existence of unpaired electrons. The simplest type of magnetism, paramagnetism, is often demonstrated in introductory chemistry courses by observing the behavior of liquid oxygen in a magnetic field. As a result of the presence of two unpaired electrons in the O_2 molecule, the liquid is attracted to a strong magnet, and if a large horseshoe magnet is used, the liquid oxygen appears to hover, trapped between the poles of the magnet *(10)*.

A family of solid manganese oxides can be used to establish a connection between the formal oxidation state of the manganese atoms in the solids, their electron configurations and number of unpaired electrons, and their relative response to a magnetic field.

Demonstration 2.2. Paramagnetism

Materials

MnO_2
Mn_2O_3
$KMnO_4$
Strong magnet such as a rare earth or cow magnet (*see* Supplier Information)
Empty gelatin pill capsules (available from pharmacies or health food stores)
Overhead projector and screen

Procedure

- Prior to the demonstration, place each solid to be studied in a separate pill capsule. Use about 0.01 mol (simply filling the capsules or using equimolar amounts gives the same qualitative results).
- To do the demonstration, lay the capsules end-to-end in a lengthwise row (with gaps in between them) on the overhead projector.
- Place the magnet on the projector's glass surface and slowly approach one of the capsules with the magnet. Note the effect of the magnet on the capsule (e.g., no attraction, slight attraction when the magnet is very close, or the capsule rolls toward the magnet).
- Repeat the procedure with each capsule. Rank the relative strengths of the interactions. The strength of the interaction will increase as the number of unpaired electrons associated with the manganese atoms increases. This result matches the order of the magnetic moments for these compounds, as determined by more quantitative techniques, Table 2.2.

Variation (requires enclosed analytical balance)

- Place the magnet on a stack of foam cups so that the magnet is near the roof of the balance (*see* Figure 2.10). **Caution! Maintain a sufficient distance between the magnet and the balance electronics. The magnet should not be placed on the balance pan or permanent damage to the balance may result.**
- Close the doors and tare the balance.
- Place the sample on the outside of the balance enclosure and observe the decrease in weight as the magnet is attracted to the sample. More unpaired electrons give larger weight changes.

Table 2.2. Magnetic Moments

Formula	Formal Mn Oxidation State	Number of Unpaired Electrons, n	$\sqrt{n(n+2)}$	Magnetic Moment[a]
Mn_2O_3	+3	4	4.90	4.9
MnO_2	+4	3	3.87	3.8
$KMnO_4$	+7	0	0	0.2

[a] Room-temperature experimental magnetic moment in units of Bohr magnetons, based on quantitative weight measurements with and without a calibrated magnetic field. Most inorganic chemistry laboratory manuals give details. In the simplest case, the predicted magnetic moment is $\sqrt{n(n+2)}$, where n is the number of unpaired electrons.

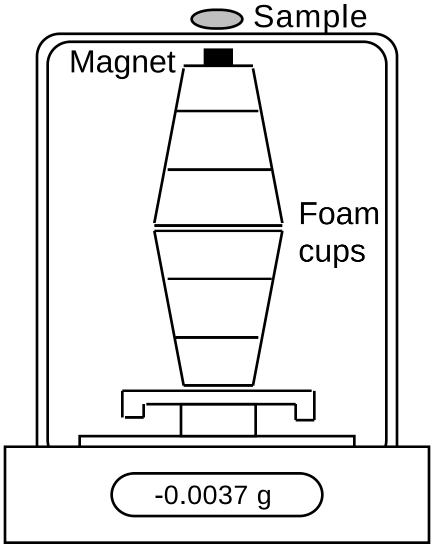

Figure 2.10. Enclosed balance used to observe the change in weight of a magnet attracted to a sample. (Based on reference 11.)

Ferromagnetism

Cooperative effects, in which many unpaired electrons communicate and interact with one another, can lead to more complex magnetic behavior in an extended solid than that observed for molecules in the gas or liquid states. An excellent example of cooperative behavior in solids is ferromagnetism, a property that is technologically important and extensively exploited in the use of permanent magnets, magnetic recording media, and transformers.

The difference between simple paramagnetism and ferromagnetism is shown in Figure 2.11. (Unpaired electrons or spins are depicted in this figure by arrows.) There are unpaired spins in a simple paramagnet (Figure 2.11A), but in the absence of a magnetic field, the spins are randomly oriented relative to one another because of thermal motion and do not interact. The application of a magnetic field to a paramagnet aligns the spins along or in opposition to the magnetic field, and the overall magnetization is small (Figure 2.11B). This property is due to a lack of communication or magnetic ordering between the spins and some thermally induced disordering of the spins. Moreover, the spins disorder when the field is removed.

In a ferromagnet, the unpaired electrons strongly communicate with one another and align (even in the absence of a magnetic field) in large regions known as magnetic domains (Figure 2.11C). The sizes of the domains vary with the material, but are quite large with respect to single atom sizes. In the absence of a magnetic field, the individual domains are ordered randomly relative to one another so that the net magnetization of a macroscopic piece of ferromagnet is small or even zero. The application of a magnetic field (Figure 2.11D) aligns all of the spins in the direction of the magnetic field, leading to a large, overall net magnetization.

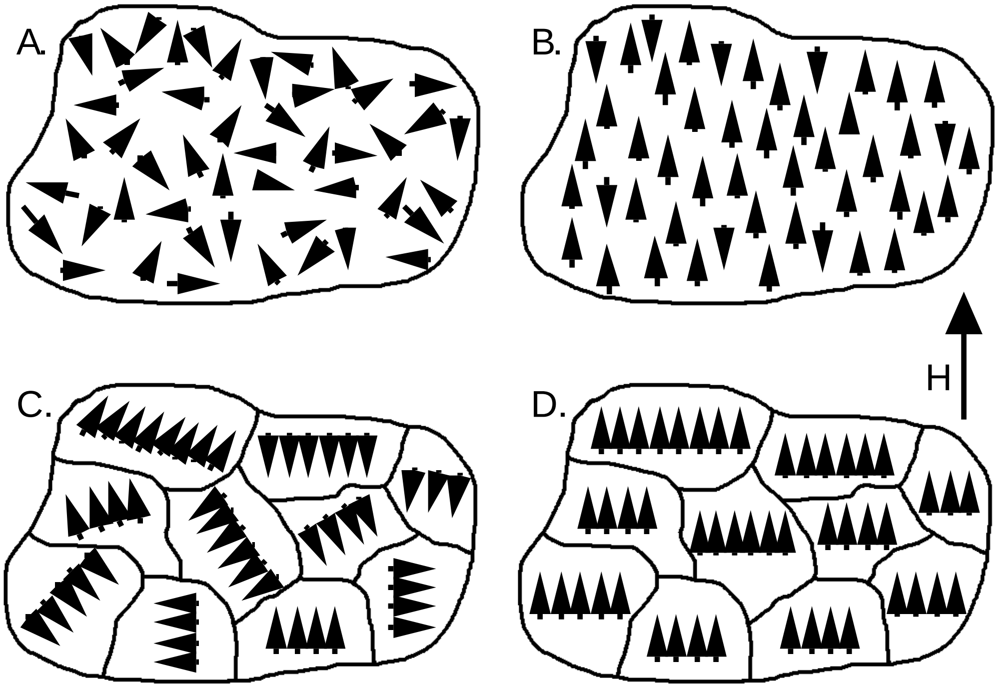

Figure 2.11. A diagram showing the orientation of electrons in (A) a paramagnetic solid in the absence of a magnetic field, H; (B) a paramagnetic solid in the presence of a magnetic field; (C) a ferromagnetic solid in the absence of a magnetic field; and (D) a ferromagnetic solid in the presence of a magnetic field.

Demonstration 2.3. A Comparison of Paramagnetism and Ferromagnetism

Materials

One or more of the gelatin capsules containing paramagnetic manganese compounds described in Demonstration 2.2
Gelatin capsule containing cobalt, nickel, or iron metal powder
Strong magnet such as a rare earth magnet
Overhead projector and screen

Procedure

- Place the gelatin capsules end-to-end in a lengthwise row on the overhead projector. Leave space between them.
- Lay the magnet on the glass overhead projector stage and slowly move it toward the long side of each of the capsules in turn. Note the response of each capsule to the magnetic field. The capsule containing the ferromagnetic cobalt (alternatively, nickel or iron) powder will produce a much more dramatic response than any of the paramagnetic manganese compounds, as the capsule jumps toward the magnet.

The technological applications of magnetic properties rely on the existence of domain walls and the ability to control the movement of the domain walls. For example, in permanent magnets, the domain walls are not easily moved. If the orientation of the spins is retained when the applied field is removed, a permanent magnet has been produced.

Ferromagnetic materials form the basis for audio and VCR tape technology. The tape itself consists of a polymer that is impregnated with crystals of γ-Fe_2O_3 or CrO_2 or a similar compound. The recording device consists of an electromagnetic head that creates a varying magnetic field as it receives signals from the microphone. The tape is magnetized as it passes through the magnetic field of the recording head. The strength and direction of the magnetization varies with the frequency of the sound to be recorded. When the tape is played, the magnetization of the moving tape induces a varying current whose signal is amplified and sent to the speakers.

Ferromagnetic materials also can form the basis for digital recording media such as computer disks. Computers store and manipulate data using binary numbers consisting of the digits 0 and 1. The letters SCN, for example, are typically represented, respectively, by the binary numbers 01010011, 01000011, and 01001110. The power of binary numbers is that their bits can be represented and processed by transistors (off represents 0; on represents 1) or stored using a variety of media that contain regions that can have one of two states. Magnetic media such as computer disks use very small domains to hold binary bits. If a region is magnetized, it represents a 1; if it is not magnetized, it represents a 0.

Recently, magnetic materials based on the garnet structure (see Experiment 14) have begun to replace traditional ferromagnetic materials. In magnetic bubble domain memory storage, the ability to move the domain walls underlies the writing capabilities in the read–write mode. Materials chemists are continuing to search for new storage media that can be written (some bits turned on) and erased (each bit turned off) quickly, that can store huge volumes of information in a small space, and that are stable and retain their information with reliability.

Laboratory. A laboratory experiment involving the preparation and characterization of a series of rare earth iron garnets with interesting magnetic properties is presented in Experiment 14.

The magnetic behavior of a ferromagnet is temperature-dependent because of the interplay of thermal energy and the stability gained by aligning the electrons in the ferromagnetic state. Ferromagnetism is an example of a solid-state phase transition (*see* Chapter 9) with a characteristic transition temperature. Above an ordering or critical temperature, known as the Curie temperature (T_{curie}), thermal energy is sufficient to break the alignment of the spins, and the material exhibits simple paramagnetism. At and below T_{curie}, the aligning forces overcome thermal randomization, the spins are locked in alignment, and the material becomes ferromagnetic. Table 2.3 lists some common ferromagnets and their Curie temperatures *(12)*.

Table 2.3. Some Ferromagnets and Their Curie Temperatures

Material	T_{curie} (K)
Fe	1043
Co	1388
Ni	627
Gd	293
$CrBr_3$	37
EuO	77
EuS	16.5

Demonstration 2.4. The Curie Point of Nickel

Materials

Nickel spheres (6–16-mm diameter; Aldrich 21,577-5)
Common bar magnet or cow magnet. *See* Supplier Information.
Meker burner
Canadian nickel minted prior to 1982 (optional)
Tongs (optional)
Heat-proof pad (optional)

Procedure

- Place one or more nickel spheres in the grating that is at the top of a Meker burner.
- Move the magnet near a sphere. The attraction between them will allow the sphere to be picked up by the magnet.
- Remove the nickel sphere from the magnet and return it to the grating.
- Light the burner with the nickel sphere on top.
- Wait 30–60 seconds and turn off the burner. Move the magnet near a sphere. If the sphere is above the Curie temperature (627 K) of nickel, it will no longer be ferromagnetic and will not be strongly attracted to the magnet. As the sphere cools below the Curie temperature, the ferromagnetism will return, and the nickel sphere can once again be picked up by the magnet. **Warning! The nickel sphere will be hot.**

Variation

Canadian nickels minted prior to 1982 (these contain pure nickel, while nickels dated since 1982 contain 75% Cu and 25% Ni) can be used in place of nickel spheres. If a Canadian nickel is used, hold it in the flame with tongs. Remove it periodically, set it on a heat-proof pad, and note its interaction with the magnet.

Demonstration 2.5. The Curie Point of Iron (modified from reference 13)

Materials

Small magnet
String
Ring stand and clamp
28-gauge steel wire (available at hardware store, may be galvanized)
Two nails

Small block of wood
Variable voltage supply with leads

Procedure

- Pound the nails into the block of wood about 3 inches apart.
- Stretch a section of the wire across the nails and wrap it tightly just below the heads of the nails. Make sure it is taut.
- Fasten the magnet to the string (perhaps with another magnet) and suspend from a clamp on a ring stand. Figure 2.12 shows a picture of the apparatus. Arrange the magnet so that it is pulled toward, but does not touch, the steel wire. If the magnet is touching the wire, the magnet will act as a heat sink and the wire will not reach the Curie temperature at the point of contact.
- Make sure the variable voltage supply is off and unplugged. Attach the leads from the voltage supply to the base of the nails.
- Turn the voltage supply to the zero setting and plug it in. Slowly increase the voltage *while watching the wire. The maximum voltage needed is 5–6 V.* The wire will begin to turn orange, and when the Curie temperature is reached, the magnet will fall away from the wire. Immediately return the voltage to zero and watch the magnet return as the wire cools. Repeat several times. **Warning: The wire will be hot. Too high a voltage or continued current flow will melt the wire. Do not touch the nails or wire while the circuit is energized.**

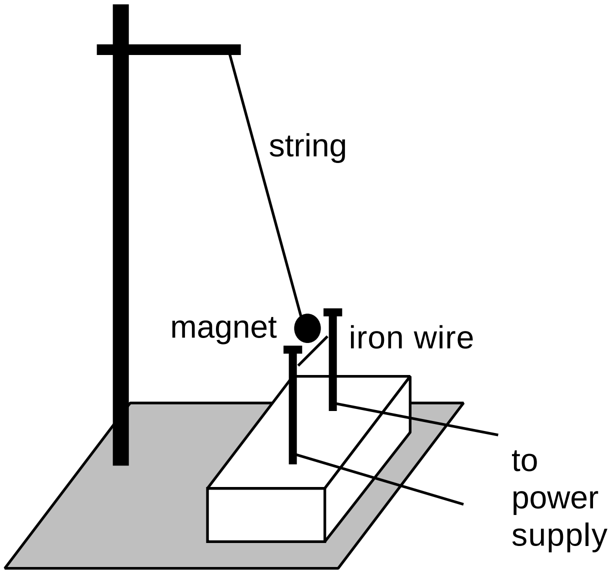

Figure 2.12. The apparatus for the demonstration on the Curie point of iron.

Many other extended solids exhibit interesting magnetic behavior with a characteristic onset temperature. The magnetic ordering can become quite complex, depending on the composition of the solid and the three-dimensional structure in which the atoms are arranged.

Ferrofluids

In recent years, researchers have prepared ferrofluids, which have the fluid properties of a liquid and the magnetic properties of a solid *(14).* The ferrofluids actually contain tiny particles (~100-Å diameter) of a magnetic solid suspended in a liquid medium.

Ferrofluids were originally discovered in the 1960s at the NASA Research Center, where scientists were investigating different possible methods of controlling liquids in space *(15).* The benefits of a magnetic fluid were immediately obvious: The location of the fluid could be precisely controlled through the application of a magnetic field, and, by varying the strength of the field, the fluids could be forced to flow. Researchers have prepared ferrofluids containing small particles of ferromagnetic metals, such as cobalt and iron, as well as magnetic compounds, such as manganese zinc ferrite, $Zn_xMn_{1-x}Fe_2O_4$. ($0 \le x \le 1$; this is a family of solid solutions, which are described in Chapter 3). But by far, the most work has been conducted on ferrofluids containing small particles of magnetite, Fe_3O_4.[2]

Ferrofluids containing magnetite can be prepared by combining the appropriate amounts of an Fe(II) salt and an Fe(III) salt in basic solution, a combination that causes the mixed valence oxide, Fe_3O_4, to precipitate from solution:

$$2\,FeCl_3 + FeCl_2 + 8\,NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8\,NH_4Cl$$

However, the particles of magnetite must remain small in order to remain suspended in the liquid medium. To keep them small, magnetic and van der Waals interactions must be overcome to prevent the particles from agglomerating. Thermal motion of magnetite particles smaller than 100 Å in diameter is sufficient to prevent agglomeration due to magnetic interactions.

The van der Waals attraction between two particles is strongest when the particles approach each other at close distances. Therefore, one method of preventing agglomeration due to van der Waals forces is to keep the particles well separated. This separation can be accomplished by adding a surfactant to the liquid medium; for example, oleic acid can be used for oil-based ferrofluids. The surfactant is a long-chain hydrocarbon with a polar head that is attracted to the surface of the magnetite particle; thus a surfactant coating is formed on the surface. The long chains of the tails act as a repellent cushion and prevent the close approach of another magnetite particle (Figure 2.13).

---

[2] Magnetite is ferrimagnetic: There are two spin sets in opposing directions that do not cancel and therefore leave a net spin.

A. $2\ FeCl_3 + FeCl_2 + 8\ NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8\ NH_4Cl$

B. Add *cis*-oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, in oil.

C. Remove water:

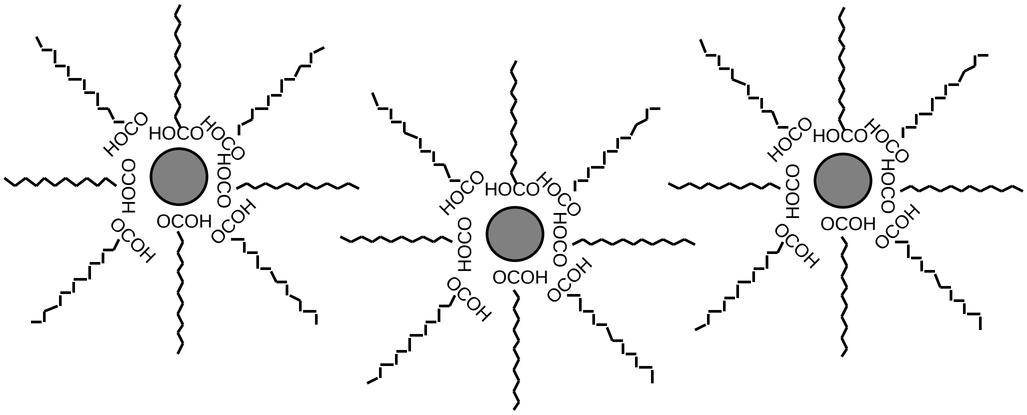

Figure 2.13. The preparation of ferrofluids: (A) the synthetic conditions for production of Fe_3O_4(s); (B) addition of surfactant; and (C) removal of water to give small particles of Fe_3O_4 (shaded circles) stabilized by the interaction of the polar ends of the oleic acid molecules with the magnetite particles, and by the interaction of the nonpolar ends of the oleic acid molecules with the oil serving as the liquid medium.

Demonstration 2.6. Ferrofluids

Materials

- A mineral oil-based ferrofluid with a saturation magnetization of 400 gauss obtained from Ferrofluidics[3]
- Strong magnet (cow magnet, bar magnet, or rare earth magnet)
- Long test tube
- Petri dish

Caution! The ferrofluid causes stains and is difficult to remove from skin and fabrics. Keep the fluid off the magnet. It is virtually impossible to remove ferrofluid after direct contact with a strong magnet.

---

[3] Ferrofluidics sells ferrofluids containing magnetite in a variety of liquid media (hydrocarbon, water, mineral oil) and with a variety of magnetic strengths. *See* Supplier Information.

Procedure

- Transfer a small amount of ferrofluid to a long test tube or other long glass tube.
- Using a strong magnet placed outside of the tube, drag the ferrofluid up the side wall of the glass tube. This step demonstrates effectively how the position of the ferrofluid can be controlled with a magnetic field. (Upon removal of the magnet, the ferrofluid tends to coat the glass. Several hours may be required for the ferrofluid to drain sufficiently so that the demonstration may be viewed again in the same tube.)
- Pour a small amount of ferrofluid into a Petri dish, so that the bottom of the dish is covered.
- Bring a strong magnet up *underneath* the Petri dish. Spikes of ferrofluid will rise up from the surface. As the magnet is brought closer to the *bottom* of the Petri dish, first one spike appears, then several spikes appear, until the spikes appear to close-pack (Chapter 5), with any given spike having six nearest neighbors arranged in a regular hexagon. The pattern of spikes appears because the ferrofluid arranges itself along the magnetic field lines of the magnet (as do iron filings). The number of visible spikes reflects the strength of the magnetic field and the surface tension of the medium.
- Place a cow magnet horizontally *underneath* the Petri dish. A pattern of spikes will appear at the two poles of the magnet (*see* Figure 2.14). If no spikes are seen, try using a stronger magnet, as this behavior depends on both the strength of the magnetic field and the magnetic strength of the ferrofluid.
- Place a penny in the ferrofluid in the Petri dish. The penny sinks to the bottom.
- Bring a strong magnet up *underneath* the container. The attraction of the ferrofluid for the magnet forces the penny up and out of the ferrofluid. Repeat this demonstration with water to show that the magnet is not pushing the penny up.

Demonstration 2.7. The Ferrofluidics Bottle Cell

Materials

Bottle cell (Ferrofluidics sells these for demonstration purposes. They consist of a sealed tube that contains a small amount of the dark brown ferrofluid and an aqueous medium. These two liquids occupy the full volume of the tube.)
Strong magnet
Large crystallizing dish, one-third full of water

Overhead projector

Procedure

- Drag the magnet up the side of the bottle cell. The ferrofluid will be attracted to the magnet. (This step basically repeats the first part of the previous demonstration, but in the bottle cell the ferrofluid falls to the bottom of the glass tube immediately upon removal of the magnet so that the demonstration can be shown repeatedly.)
- On an overhead projector, place the bottle cell lengthwise in the crystallizing dish so that it is under water; it may need to be held or taped down.
- Bring the magnet up to the side of the cell. The ferrofluid will be attracted to the magnet and the spiking phenomenon described in the previous demonstration will be visible in profile. (If the bottle cell is not under water, the rounded sides of the bottle cell scatter light and make it difficult to effectively project an image of the ferrofluid.)
- In our experience, a fresh bottle cell works best; the performance deteriorated over several weeks.

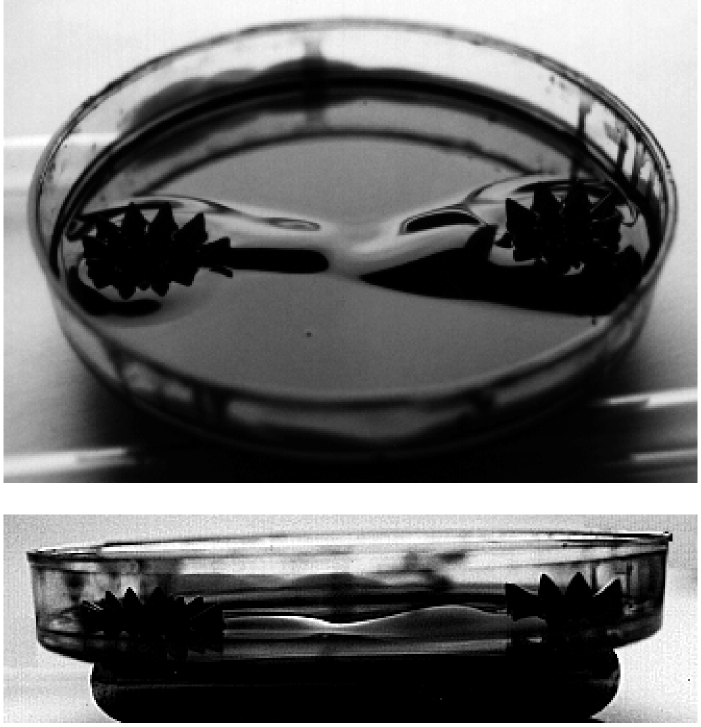

Figure 2.14. Top and side views of the magnetic spiking phenomenon observed when a cow magnet is placed beneath a Petri dish containing a ferrofluid. The ferrofluid aligns with the magnetic field lines of the magnet to produce the spikes.

Although the array of spikes on the surface of the ferrofluid is spectacular, this property is not particularly useful. However, ferrofluids have found a wide variety of applications *(16, 17),* including use in rotating shaft seals. A ferrofluid can behave as a liquid O-ring where a rotating shaft enters either a low- or high-pressure chamber. The ferrofluid is held in place by permanent magnets and forms a tight seal, eliminating most of the friction produced in a traditional mechanical seal. These rotating shaft seals are found in rotating anode X-ray generators and in vacuum chambers used in the semiconductor industry. Ferrofluid seals are used in high-speed computer disk drives to eliminate harmful dust particles or other impurities that can cause the data-reading heads to crash into the disks.

Another application of ferrofluids is in improving the performance of loudspeakers. In a loudspeaker, electric energy is sent through a coil located in the center of a circular permanent magnet. The magnetic field induced by the electric energy causes the coil to vibrate and thus produces sound and heat. Bathing the electric coil in a ferrofluid, which is held in place by circular permanent magnets, dampens unwanted resonances and also provides a mechanism to dissipate heat from excess energy supplied to the coil. Both of these factors lead to an overall improved sound quality.

Finally, there is much hope for future biomedical applications of ferrofluids. For example, researchers are attempting to design ferrofluids that can carry medications to specific locations in the body through the use of applied magnetic fields. Other ongoing work is investigating the use of ferrofluids as contrast agents for magnetic resonance imaging (MRI).

Electrorheological Fluids

Like ferrofluids, electrorheological (ER) fluids *(18)* comprise suspensions of particles in a liquid medium, but their operation depends on electric rather than magnetic interactions. As noted in Chapter 1, ER fluids are “smart materials,” whose viscosity can be tuned by an applied electric field.

ER fluids consist of a colloidal suspension of polarizable particles in a nonpolar solvent. These high-tech materials can be created from low-tech, inexpensive compounds, such as flour suspended in vegetable oil; or alumina or silica suspended in silicone oil.

The mechanism by which ER fluids operate is depicted in Figure 2.15. The presence of a strong electric field formed between two electrodes can induce dipoles in the suspended particles (one end of the particle acquires positive charge, the other end negative charge) that cause them to align with one another in an orientation that is parallel to the applied electric field. The particles stick to each other, much like damp grains of sand, and a fibrous structure is created within the medium that can cause the viscosity of the suspension to be increased by factors approaching 10^5. The dipoles disappear when the electric field is turned off, and the suspension regains its liquid nature. Completing the analogy to sand, this system would be akin to being able to remove the water rapidly from wet sand and thus restore its ability to be poured easily. Figure 2.16 illustrates the change in viscosity accompanying application of a strong electric field to the ER fluid.

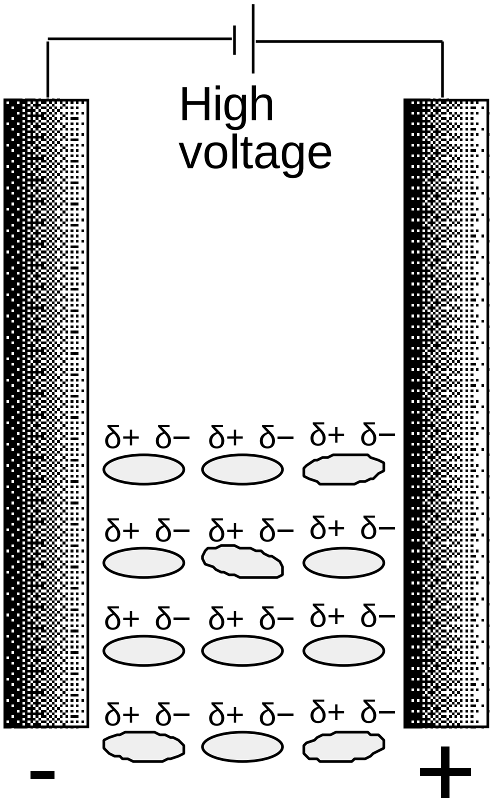

Figure 2.15. When an electrorheological (ER) fluid is placed in a strong electrical field, an induced dipole is created on the particles of the fluid. The particles stick to each other, and the fluid is suspended between the electrodes as long as the field is maintained.

The speed with which ER fluids can respond to applied electric fields is sufficiently fast that they are being considered for use in automobile shock absorbers and clutches. Figure 2.17A illustrates the design of a shock absorber that offers active control over automobile vibrations. Figure 2.17B demonstrates how an automobile clutch might benefit from ER fluids.

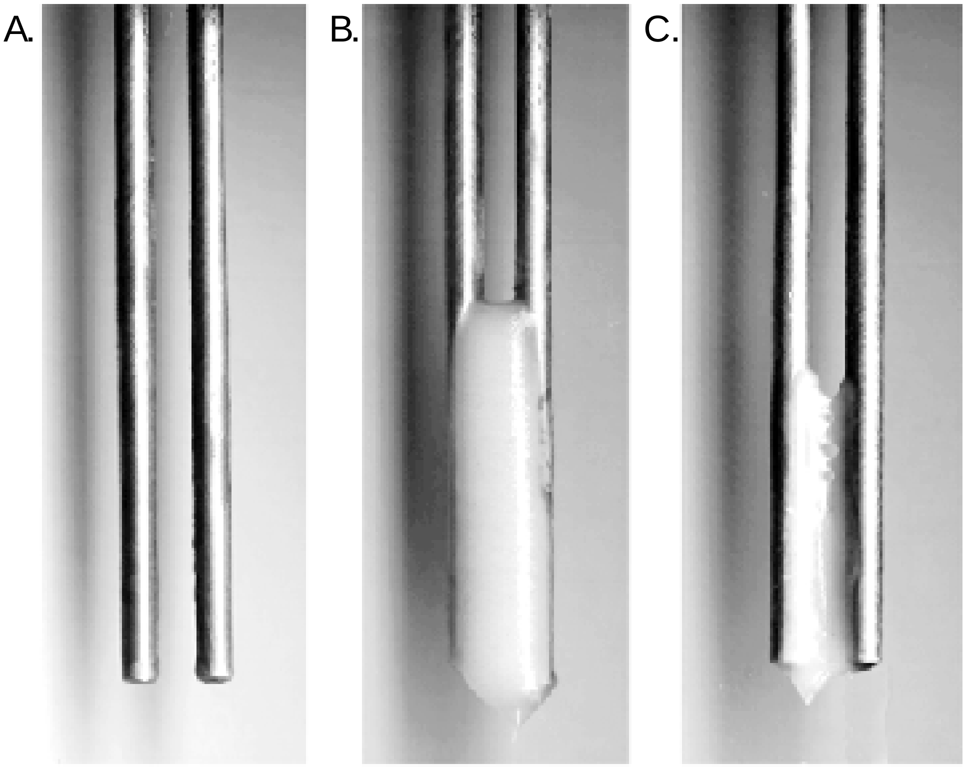

Figure 2.16. (A) The two electrodes with which an electric field can be applied to an ER fluid. No ER fluid is present. (B) When the electrodes are dipped in an ER fluid, flour in corn oil, and a high voltage (~10^4 V/cm) is applied, dipoles are induced in the particles. A fibrous network is formed suspending the material between the electrodes. (C) When the electric field is turned off, the viscosity of the medium decreases and the ER fluid drains off the electrodes.

Piezoelectric Crystals

Even though solids are electrically neutral, they may consist of electrically charged species like the anions and cations that comprise salts (NaCl, for example); or of numerous dipole moments that result from the presence of polar bonds formed between atoms of different electronegativities that make up the solid (quartz or SiO_2, for example). These regions of localized charge concentration notwithstanding, often no net electric dipole moment exists in such materials because the arrangements of the atoms or ions lead to a cancellation of individual dipole moments or charges. A molecular analogy might be to the nonpolar nature of silicon tetrafluoride: despite having individual polar Si–F bonds, the tetrahedral geometry of SiF_4 causes the vector sum of the four individual Si–F dipoles to be zero. Equivalently, because the centers of partial positive and negative charge for the collection of the four individual dipoles coincides, there is no net dipole moment.

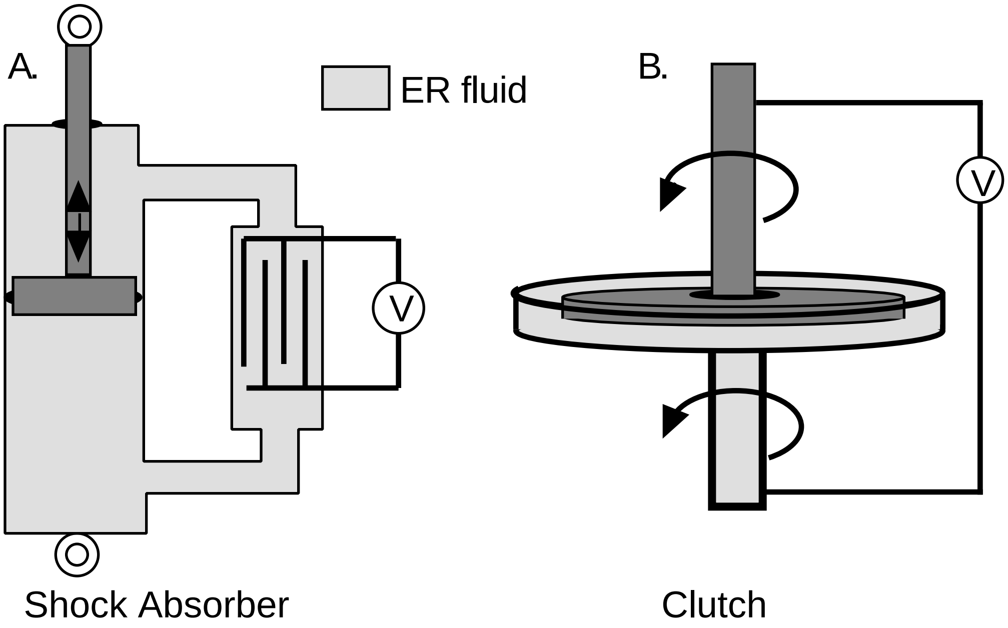

Figure 2.17. (A) A shock absorber damps vibrations by moving a piston (dark shading) through a compressible fluid. In the shock absorber shown, varying the voltage, V, varies the flow of ER fluid through a bypass valve to provide variable cushioning. (B) A clutch mechanically couples two moving parts. In the clutch shown, varying the voltage, V, varies the viscosity of the ER fluid, either letting one plate turn freely or connecting it to the other plate.

Materials like quartz are piezoelectric because they have the ability to develop a net dipole moment if they are mechanically deformed in particular directions relative to the arrangement of atoms in the crystal; and to be mechanically deformable by an electric field having an appropriate direction relative to the atoms in the solid. Both of these effects are reversible.

Figure 2.18 illustrates the mechanically induced creation of a net dipole moment where none is present initially. Shown in the figure are anions and cations from a section of a larger crystalline salt. In their natural state, the geometric centers of the three anions and three cations coincide, and no net dipole moment is expected or observed. If the salt is compressed as shown, however, the ions are displaced in the indicated directions, and the geometric centers of positive and negative charge no longer coincide: a net dipole moment has been generated and will disappear upon release of the pressure. This displacement of electron density corresponds to a voltage that develops across the opposite crystal faces or to a usable electric current if a wire is connected to the opposing crystal faces, because the net movement of negative charge in one direction is reinforced by the net movement of positive charge in the opposite direction.

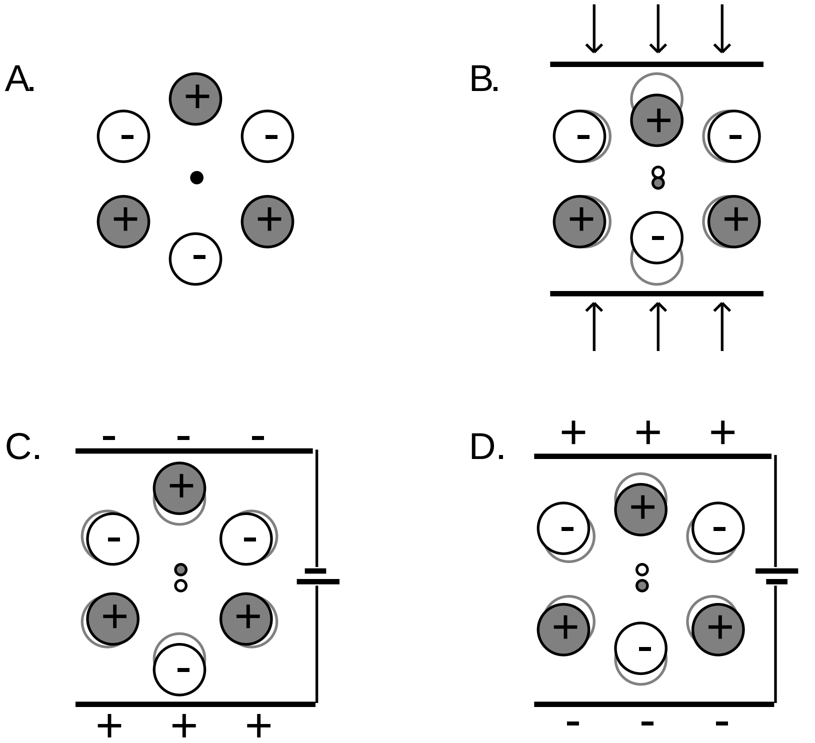

Figure 2.18. A two-dimensional model for a piezoelectric crystal. (A) In its equilibrium shape, the centers of positive and negative charge in the crystal coincide. The black dot in the center of the picture represents these centers of charge. (B) As the crystal is compressed, the ions move as indicated, causing the center of positive charge (small gray dot) to separate from the center of negative charge (small white dot). This separation generates a net dipole moment in the crystal and a movement of charge, that is, a current. As the pressure on the crystal is released, current flows in the opposite direction. (The original ion positions are shown in outline). (C) If a voltage with the indicated polarity is applied, the atoms move as shown, and the result is a net expansion of the crystal. (D) When a voltage of the opposite potential is applied, the atoms move as indicated, and the result is a net compression of the crystal. (Figure based on reference 19.)

Figure 2.18 also shows how an applied voltage can mechanically deform such a crystal. When a voltage is applied across the opposing faces shown, the cations will move toward the negative electrode and the anions toward the positive electrode. With one direction of applied voltage, the electric field compresses the crystal; reversing the direction of the applied voltage causes the ions to move in the opposite direction and thus makes the crystal expand.

Quartz is a piezoelectric material that is commonly used in watches and the strikers of lighters. In watches, an oscillating electric field applied to a quartz crystal makes the quartz crystal oscillate at a natural resonance frequency that is dependent on the size of the crystal. The vibrations of this very specific frequency are counted and used to keep the watch on time.

In strikers, both the creation and loss of the electric dipole correspond to large changes in the electric field. Thus, either rapid squeezing of the piezoelectric crystal or rapid release of the pressure applied to the crystal can cause sparking in the nearby combustible gas and ignite it. The sparking action occurs with the crystal in a commonly available cigarette lighter.

Demonstration 2.8. The Piezoelectric Effect

Materials

A piezoelectric lighter (available from chemical suppliers such as Aldrich or Flinn Scientific) or **empty** Scripto cigarette lighter with no fuel remaining

Procedure

- Squeeze the trigger to cock a spring-loaded hammer.
- When the trigger reaches the end of its cycle, the spring is released and the hammer strikes the piezoelectric crystal.
- A spark that travels several millimeters in air is observed, corresponding to ~10 kV.

References

1. Braun, R. D. *J. Chem. Educ.* **1992**, *69,* A90.
2. Binnig, G.; Smith, D. P. E. *Rev. Sci. Instrum.* **1986**, *57*, 1688.
3. Eigler, D. M.; Schweizer, E. K. *Nature (London)* **1990**, *344*, 524.
4. Wenjie, L.; Virtanen, A.; Penner, R. M. *J. Phys. Chem.* **1992**, *96*, 6529–6532.
5. Atkins, P. W. *Physical Chemistry,* 4th ed.; Freeman: San Francisco, CA, 1990, p 296. See also Conant, J. B. *Harvard Case Histories in Experimental Science;* Harvard University Press: Cambridge, MA, 1957, p 305.
6. Atkins, P. W. *Physical Chemistry,* 4th ed.; Freeman: San Francisco, CA, 1990; Chapter 20.
7. *Specific Heat: Metallic Elements and Alloys;* Thermophysical Properties of Matter Vol. 4, ISI/Plenum: New York, 1970.
8. *Specific Heat: Nonmetallic Solids;* Thermophysical Properties of Matter Vol. 5; ISI/Plenum: New York, 1970.
9. Guinier, A.; Jullien, R. *The Solid State: From Superconductors to Superalloys;* International Union of Crystallography: Oxford, England, 1989, p 34.
10. Shakhashiri, B. Z.; Dirreen, G. E.; Williams, L. G. *J. Chem. Educ.* **1980**, *57,* 373.
11. McHale, J.; Schaeffer, R.; Salomon, R. E. *J. Chem Educ.* **1992**, *69*, 1031.
12. Ashcroft, N. W.; Mermin, N. D. *Solid State Physics;* Saunders College: Philadelphia, PA, 1976; p 697.

13. *Exploratorium Science Snackbook;* Doherty, P.; Rathjen, D., Eds.; Exploratorium Teacher Institute: San Francisco, CA, 1991; pp 34–35.
14. Charles, S. W.; Popplewell, J. In *Ferromagnetic Materials*; Wohlfarth, E. P., Ed.; North Holland Publishing Co.: Dordrecht, Netherlands, 1980; Vol. 2, pp 509–559.
15. Papell, S. S. U.S. Patent 3,215,572, November 2, 1965.
16. Popplewell, J.; Charles, S. *New Sci.* September 25, 1980, 332–334.
17. Rosensweig, R. E. *Sci. Am.* October 1982, 136–145.
18. Halsey, T. C. *Science (Washington, DC)* 1**992**, *258*, 761.
19. Holden, A.; Singer, P. *Crystals and Crystal Growing*; Anchor: Garden City, NY, 1960.

Additional Reading

- Binnig, G.; Rohrer, H. *Rev. Mod. Phys.* **1987**, *59*, 615.
- Guinier, A.; Julien, R. *The Solid State: From Superconductors to Superalloys*; Oxford University Press: Oxford, England, 1989.
- Raj, K.; Moskowitz, R.; *J. Magn. and Mag. Mat.* **1990**, *85*, 233–245.
- Holden, A.; Singer, P. *Crystals and Crystal Growing*, Anchor: Garden City, NY, 1960.

Acknowledgments

The section on the scanning tunneling microscope is based on a description supplied by Robert Hamers, University of Wisconsin—Madison, Department of Chemistry, Madison, Wisconsin.

The section on heat capacities was written with assistance from James Skinner, Gil Nathanson, and Hyuk Yu, Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin.

The section on magnetic properties was written with assistance from Joel Miller, Department of Chemistry, University of Utah, Salt Lake City, Utah.

The section on ER fluids benefited from comments by Daniel Klingenberg, University of Wisconsin—Madison, Department of Chemical Engineering, Madison, Wisconsin.

We thank Reginald Penner, University of California at Irvine, Department of Chemistry, for supplying a copy of the photograph in Figure 2.8.

We thank Z. S. Teweldemedhin, R. L. Fuller, and Martha Greenblatt, Department of Chemistry, Rutgers University, for suggesting the compounds used in Demonstration 2.2, and for determining their magnetic moments.

Exercises

1. The STM trace of the surface of a niobium crystal is identical in dimension and arrangement of the atoms to that of a tantalum crystal. Why is the density of tantalum equal to 16.6 g/cm^3 while that of niobium is only 8.57 g/cm^3?

2. The radius of a tungsten atom is estimated to be 137 pm. What is the diameter in meters, centimeters, and angstrom units of a perfect STM tip that terminates in a single atom of tungsten?

3. Estimate the molar heat capacity of the following compounds:
   a. RbCl, CaS, MnO, or any other 1:1 salt
   b. MgF_2, $MnCl_2$, TiO_2, Na_2S, or any other 2:1 or 1:2 salt
   c. AlF_3, $FeCl_3$, Li_3P, or any other 1:3 or 3:1 salt
   d. Al_2O_3, Ca_3P_2 or any other 2:3 or 3:2 salt

4. Estimate the gram heat capacity (the amount of heat required to raise the temperature of 1 g of a substance by 1K, also called the specific heat) of any of the substances in Table 2.1.

5. Use a metal from Table 2.1 and its heat capacity for the following problem. A 100-g sample of a metal is heated to 100 °C in boiling water. The sample is then placed in 100.0 g of cool water at 23.4 °C. What will be the final temperature of the water and the metal, assuming no loss of heat to the surroundings?

6. A 70.0-g piece of metal at 80.0 °C is placed in 100.0 g of water at 22.0 °C. The metal and the water come to the same temperature at 26.4 °C. Estimate the approximate atomic weight of the metal, assuming no loss of heat to the surroundings.

7. Sodium bromide dissolves in water but not in ethyl alcohol. Describe an experiment using known masses of aluminum, NaBr, and ethyl alcohol, along with water, that could be used to determine the heat capacity of NaBr.

8. Sketch an STM trace of the front face of any unit cell from Chapter 3.

9. How far does an STM tip traverse in scanning a row of 400 nickel atoms? The radius of a nickel atom is 1.24 Å.

10. Gas pressures of 10^{-10} torr are needed to study metal surfaces for periods of hours without contamination. However, gases with this low a pressure still contain tremendous numbers of molecules. How many molecules are present in 1.0 mL of a gas with a pressure of 1.0×10^{-10} torr at a temperature of 23 °C?

11. Calculate the molar heat capacity of a monatomic gas in Flatland, a country in a hypothetical universe with only two dimensions.

12. If the specific heat of copper metal is 0.38 J/g-°C, estimate the specific heat of silver metal.

13. Given the following measurements for the gram specific heat, calculate and compare the molar heat capacities.

Element	Gram heat capacity, J/g-°C
Bi	0.120
Zn	0.388
Fe	0.460
S	0.787

14. Elemental iron is ferromagnetic, yet an iron nail does not attract iron filings.
    a. Explain.
    b. If, however, a magnet is rubbed over the surface of a nail, the nail will attract iron filings. Why?

15. Although the formula weight of the salt calcium oxide and the atomic weight of elemental iron are about the same, the specific heat of calcium oxide in joules per gram-degree Celsius is twice as large as that of iron. Why?

16. Compare the solids VO and V_2O_5 in their attraction to a magnetic field.

17. Trace the energy path in a piezoelectric lighter, starting from the chemical energy used to move the trigger.

18. Propose a new use for an electrorheological fluid.