# Ferrofluid

*Teacher Materials (includes Student Materials)*

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Can be found in the July 1999 issue of the Journal of Chemical Education.
Ferrofluids

Curriculum Suggestions

Sample Lesson Plan

Ferrofluid Overview

Ferrofluids

Ferrofluid Teacher Notes

Ferrofluid Student Notes

Demonstration 1 (Instructor Copy)

Investigation 1 (Student copy)

Investigation 1 (Instructor copy)

Investigation 2 (Student copy)

Investigation 2 (Instructor copy)

Experiment 1 (Student copy)

Experiment 1 (Instructor copy)

Ferrofluid Review Questions (Student Copy)

Ferrofluid Review Questions (Instructor Copy)

Ferrofluid Assessment (Student copy)

Ferrofluid Assessment (Instructor copy)

Appendix A: Magnetic Properties of Magnetite

Appendix B: Instructions for Building the Magnetite Structure
CURRICULUM SUGGESTIONS

TOPICS

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<td>Magnetism</td>
<td>Nanoparticles</td>
</tr>
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OVERVIEW

This material could be used to introduce empirical formulas, ionic bonding considerations, and stoichiometric relationships. Another possible focus is on the magnetic character of magnetite and an explanation of the spiking behavior of the ferrofluid. Explanations of magnetism hinge on electron configurations and thus to basic ideas from quantum mechanics. The surfactant employed provides an opportunity to discuss hydrophobic and hydrophilic interactions. Ferrofluids make an important connection to nanotechnology, as the magnetic particles that are produced are typically on the order of 100 angstroms (10nm) in size. Particles in this range have a large surface-to-volume ratio that can in some cases dramatically influence their properties. In this case, the particles have a characteristic response to a magnet that leads them to be described as superparamagnetic.

SUGGESTIONS

Investigation 1-----Could be used to provide a laboratory framework within which to discuss electron configurations, orbital diagrams, and magnetic behavior.

Investigation 2-----Could be used to teach about ionic solids and crystal structure, which are often included in a unit on the phases of matter. The investigation also provides a means for determining empirical formulas.

Experiment 1-------Provides an opportunity to determine the stoichiometric mole ratio between reactants in units that deal with chemical formulas and stoichiometry. Extensions might include trying to synthesize ferrofluids using other transition metal ions such as manganese, cobalt and nickel.
SAMPLE LESSON PLAN

PREFACE

This module could stand alone with a scope that is limited to understanding the properties and uses of ferrofluids. As such it would act as a technology supplement to the standard chemistry curriculum and the following lesson plan would fulfill that objective. If, however, the module were to be used in conjunction with the topics included in the curriculum suggestions, then the lesson plan below might be considered as a framework from which an overall plan may be constructed.

DAY 1
Conduct Demonstration 1 to introduce the topic of ferrofluids as well as to observe and explain some of their unique properties. Use the follow-up questions in conjunction with the background information for this unit to facilitate this introduction.

DAY 2
Have students do Investigation 1. Allow the students ample opportunity to explore the properties of the fluid and to ponder the follow-up questions. If questions arise that would necessitate further experimentation, try to provide the time necessary to do so.

DAY 3
Discuss the results of Investigation 1. It might be a good idea to further demonstrate close-packed arrangements using marbles in a Petri dish on the overhead projector or other such demonstrations.

DAY 4
Have students perform Investigation 2.

DAY 5
Discuss Investigation 2. It will probably be necessary to have the models available during the class discussion so that you can assist in counting the number of atoms occupying the various sites in these structures. Pre-lab Experiment 1.

DAY 6
Have students carry out Experiment 1.

DAY 7
Discuss Experiment 1 and complete the discussion of ferrofluids by presenting some of their applications and asking the students for any others they may have thought about as they conducted their work.

DAY 8
Use the In-Class Discussion Questions as a review of the unit.

DAY 9
Unit Exam (See the Ferrofluid Assessment at the end of the unit.)
FERROFLUIDS

Overview

This module based on ferrofluids is intended to provide students with an opportunity to develop chemical formulas and stoichiometric relationships. The production and properties of ferrofluids are controlled by chemistry. Once prepared, they have the captivating property of exhibiting "spikes" when placed in the proximity of a strong magnet. Ferrofluids are easy to synthesize, and the procedures used in their synthesis creates a framework within which to discuss a variety of chemical and physical concepts. Ferrofluids are increasingly being used as damping devices for high-resolution speakers, rotating shaft seals in computer hard disk drives, and in a similar capacity in reduced gravity environments like those encountered by satellites. Biomedical applications such as site-controlled medication are currently being investigated.

Ferrofluids consist of a colloidal suspension of magnetic nanoparticles, typically magnetite, in a liquid medium such as paraffin oil or water. Investigations and demonstrations in this module explore the structure of magnetite, using the ICE solid state model kit. From its inverse spinel structure, the formula of magnetite can be determined and its magnetic properties discussed. A model for understanding these properties in terms of each particle of the fluid acting as a tiny magnet can be presented, as well as a more sophisticated model that includes electron configurations, oxidation states, tetrahedral and octahedral crystal sites, surfactants, and magnetic domains. An experiment concluding the module allows students to determine the correct stoichiometric ratio for the production of a ferrofluid with optimal "spiking" characteristics. This unit also serves as an introduction to nanoscale materials and technologies.

Research continues into the properties and uses of these remarkable substances. It has even been suggested that the migration of fish species such as trout back to their breeding habitat may involve a ferrofluid-like substance closely surrounding a sensory nerve center in the head of the fish.
Ferrofluids

Magnetism Review

Common magnets are typically described as having a north and south pole. Similar poles (north-north or south-south) repel one another, while opposite poles attract one another (north-south or south-north). Unpaired electrons within a magnetic material are responsible for magnetic interactions. Electrons can provide contributions to magnetism through their spin angular momentum (rotation about their axes) and their orbital angular momentum. Some materials are permanent magnets and, through contact, can impart magnetic behavior to other materials.

Ferrofluids and Their Characteristics

In the 1960’s, scientists from the NASA Research Center were investigating methods for controlling liquids in space. They developed ferrofluids, which are colloidal suspensions of magnetic nanoparticles, such as Fe$_3$O$_4$, in a liquid; the nanoparticles typically have sizes of about 100 angstroms, or 10 nm. Ferrofluids respond to an external magnetic field. This enables the fluid’s location to be controlled through the application of a magnetic field. Ferrofluids can also be prepared using metals like cobalt and iron as well as magnetic compounds such as manganese zinc ferrite (Zn$_x$Mn$_{1-x}$Fe$_2$O$_4$, 0 $\leq$ x $\leq$ 1). Much research has been centered around ferrofluids that contain small particles of magnetite, Fe$_3$O$_4$. Magnetite can be produced by mixing Fe(II) and Fe(III) salts together in a basic solution. The particles must remain small and separated from one another in order to remain suspended in the liquid medium. Magnetic and van der Waals interactions must be overcome to prevent the particles from agglomerating into larger particles. Thermal motion of magnetite particles that are smaller than ~100 angstroms in size is sufficient to prevent agglomeration due to magnetic interactions. Surfactants prevent the nanoparticles from approaching one another too closely.

Surfactants and How They Work

Surfactants are added during the synthesis of ferrofluids to surround the small particles and overcome their attractive tendencies. For example, oleic acid can be added to oil-based ferrofluids. This surfactant is a long-chain hydrocarbon with a polar head that attaches itself to the surface of the magnetite particle. The long chains comprising the tails act as a repellent cushion and prevent the close approach of another particle. For this aqueous-based synthesis of ferrofluids using magnetite, Fe$_3$O$_4$, the surfactant, tetramethylammonium hydroxide, [N(CH$_3$)$_4$][OH], is used. The nanoparticles created by the synthesis are thought to be coated with hydroxide ions from the surfactant, which themselves attract a sheath of largely positive tetramethylammonium cations. This structure creates electrostatic interparticle repulsion that can overcome the van der Waals forces that would otherwise cause the particles to agglomerate.
Picture from JCE articles—also on website from lecture notes

Spikes

When a strong magnet is placed near the ferrofluid, spikes are observed. The spikes arise from the tendency of the particles to line up along the magnetic field lines to lower their energy. Surface tension of the fluid, however, limits the extent to which the particles can align themselves with the field.

Possibly the diagram & explanation from ferrofluid paper-website
http://ice.chem.wisc.edu/materials/ferrofluids.html

Uses and Capabilities

Ferrofluids have a wide range of applications. They have been used in rotating shaft seals, where they behave as a liquid O-ring. The ferrofluid is held in place by permanent magnets and forms a tight seal, reducing friction relative to that produced in a typical mechanical seal. These rotating shaft seals are found in rotating anode x-ray generators and in vacuum chambers used in the semiconductor industry. Ferrofluids are also 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 permanent magnet. Bathing the electric coil in ferrofluid dampens unwanted resonances and provides a way to dissipate heat from the excess energy supplied to the coil. This leads to better overall sound quality. Biologists such as Michael Walker, Carol Diebel, and Cordula Haugh of the Experimental Biology Group, have also been studying how ferrofluids aid in the migratory senses of animals. They have studied how trout respond to the magnetic field of the earth. Apparently a few small branches of the trigeminal nerve enter the nose of the trout. There the nerves seem to connect with some unusual cells that do not appear to be involved in the trout's sense of smell. The cells contain crystals of a mineral that have yet to be identified. It is suspected that the crystals are
magnitite. When the magnetic field is steady, spikes or action potentials are produced. If the magnetic field changes so do the spikes. This signals when the migratory process should take place. Finally, ferrofluids may be used in future biomedical applications. Researchers are attempting to design ferrofluids that can carry medication to specific locations in the body through the use of applied magnetic fields. Ferrofluids may also be used as contrast agents for magnetic resonance imaging (MRI).
DEMONSTRATION 1
Notes for the Instructor

PURPOSE

To illustrate and discuss some of the unique properties of ferrofluids prior to the student investigations that follow.

METHOD

A bottle cell will be used to demonstrate the behavior of a ferrofluid under the influence of a strong magnet. During the discussion that follows, students should be asked to explain the observations that were made.

Although a detailed discussion of the crystal structure of magnetite is not necessary, the fact that it is generally composed of particles of magnetite (Fe₃O₄) that are ferrimagnetic and nanoscale in size (approximately 100 angstroms or 10nm) should be mentioned. Further topics for discussion might include colloidal suspensions, surfactants, and magnetic domains.

MATERIALS

Bottle cell (Available commercially from Educational Innovations)

Strong magnet

Crystallizing dish large enough to hold the cell

Overhead projector

PROCEDURE

1. Drag the magnet up the side of the bottle cell. The ferrofluid will be attracted to the magnet, demonstrating the magnetic properties of the fluid.

2. Tape the cell to the bottom of a crystallizing dish, add water until the cell is entirely submerged, and place the assembly on an overhead projector.

3. With the overhead projector on, hold the magnet beneath the surface of the water in the dish and move it up to the side of the cell. The fluid will be attracted to the magnet and the “spiking phenomena” will be observed in profile.
FOLLOW-UP QUESTIONS

Either during or after the demonstration the following questions can be addressed.

1. The bottle cell consists of a dark brown fluid suspended in an aqueous medium. What are some of the properties of the darker fluid?

   Answers will include: (1) it is a liquid (fluid); (2) it is denser than water; (3) it is not miscible with water; and (4) it is attracted to a magnet.

2. What are some other examples of substances that are affected by a magnet?

   The most common response will surely include iron-containing substances, which will allow for the introduction of the terms ferromagnetic and, ultimately, ferrofluid.

3. The magnetic properties of the fluid are caused by a compound called magnetite, having the formula Fe₃O₄. At room temperature magnetite is a solid. How do we then explain the fluid nature of the dark brown substance?

   Lead the students to understand that the magnetite must be dispersed as very small particles within a medium that is not miscible with water. In other words, it is a colloidal suspension of magnetic nanoparticles, whose sizes are in the neighborhood of 100 Angstroms, in a hydrocarbon or mineral oil medium.

4. If these particles are magnetic, why don’t they agglomerate (stick together)?

   There must be something that acts as a dispersing agent (surfactant). This agent must adhere to the particles, surround them completely, and create a net repulsion between them.

5. Once the magnet has been used to cause the spiking behavior of the fluid, why don’t the spikes stay together? Why, in other words, does the fluid “relax” once the magnet has been removed?

   Depending upon the students’ knowledge of electron configurations, unpaired electrons and parallel spins, the discussion could involve those topics, or could be more simply addressed by noting that each of the particles of magnetite behaves as a tiny magnetic domain. In the presence of the magnet, the particles attempt to orient themselves in the magnetic field, but their mobility is limited by the fluid. This causes the spikes to form. In the absence of a magnetic field, and as a result of thermal agitation, the particles quickly return to a random orientation relative to one another and the spikes disappear.
Ferrofluids

Ferrofluid - a colloidal suspension of magnetic nanoparticles, typically magnetite, in a liquid medium such as paraffin oil or water

Colloid - a dispersion of particles from ~1 nm to 1000 nm in size and suspended in a fluid

Magnetite - the name of the compound, Fe₃O₄

Properties of ferrofluids
1. Magnetism - a force that can act at a distance between two materials due to properties of their electrons’ spin and orbital motions

   Ferrimagnetism - a phenomenon in which the internal magnetic moments of multiple spin sets of unpaired electrons within the domain of the solid do not completely cancel and therefore leave a net spin

   Ferromagnetism - a phenomenon in which the internal magnetic moments of unpaired electrons within a domain of the solid are aligned and act cooperatively

2. Spike - a pattern of uplifted particles that results from placing a magnet near the ferrofluid

3. They don't stick together
   Why?
   A surfactant has been added
   Surfactant - a molecular substance or salt that surrounds particles and isolates them from the attractive forces of their neighbors

4. Why aren't the spikes permanent?
   Individual particles of magnetite behave as tiny magnetic domains. Therefore, in the absence of a magnetic field and as a result of thermal agitation, the particles’ magnetic domains become randomly oriented relative to one another.

   Magnetic domain - regions where unpaired electrons strongly interact with one another and align even in the absence of a magnetic field

Unit Cells

Unit cell: a 3-D parallelepiped that, when shifted along each edge by the length of the edge, creates the entire structure of atoms in a crystal

See Appendix A Memory Metal and/or overheads
Holes- spaces created between ions or atoms in a crystal structure
For example, in magnetite there are holes formed by oxide ions - these holes provide various environments for the iron ions

What constitutes unit cells: Show examples

Parts of a unit cell
Corner atoms = 1/8 atom per unit cell
Edges atoms = 1/4 atom per unit cell
Face atoms = 1/2 atom per unit cell
Inside atoms = 1 atom per unit cell

Atoms in the unit cell - a formula that indicates the actual number of atoms of each element in one unit cell of a crystalline solid

Empirical formula - information that gives the simplest ratio between the atoms of the elements present in a compound
Ferrofluids

Ferrofluid -

_________________ - a dispersion of particles from ~1 nm to 1000 nm in size and suspended in a fluid

Magnetite - the name of the compound, __________

Properties of ferrofluids

1. ______________ - a force that can act at a distance between two materials due to properties of their electrons’ spin and orbital motions

________________ - a phenomenon in which the internal magnetic moments of multiple spin sets of unpaired electrons within the domain of the solid do not completely cancel and therefore leave a net spin

________________ - a phenomenon in which the internal magnetic moments of unpaired electrons within a domain of the solid are aligned and act cooperatively

2. ______________ - a pattern of uplifted particles that results from placing a magnet near the ferrofluid

3. they don't stick together

   Why?
   A _______________ has been added
   Surfactant –

4. Why aren't the spikes permanent?
   Individual particles of magnetite behave as _______________. Therefore, in the absence of a magnetic field and as a result of thermal agitation, the particles’ magnetic domains become _______________ relative to one another.

   _______________ - regions where unpaired electrons strongly interact with one another and align even in the absence of a magnetic field

Unit Cells
a 3-D parallelepiped that, when shifted along each edge by the length of the edge, creates the entire structure of atoms in a crystal

Holes-

For example, in magnetite there are holes formed by oxide ions - these holes provide various environments for the iron ions

What constitutes unit cells:

Parts of a unit cell
- Corner atoms = _____ atom per unit cell
- Edges atoms = _____ atom per unit cell
- Face atoms = _____ atom per unit cell
- Inside atoms = _____ atom per unit cell

Atoms in the unit cell -

Empirical formula -
INVESTIGATION 1
Notes for the Instructor

PURPOSE

To allow students to gain some knowledge about the behavior of ferrofluids.

METHOD

Supply the students with a small amount of a mineral oil-based ferrofluid and allow them to experiment with the magnetic properties of the fluid. CAUTION! Ferrofluids cause stains that are very difficult to remove from skin and fabrics. It is also imperative that the fluid be kept off of the magnet. It is almost impossible to remove the ferrofluid from a strong magnet.

MATERIALS

Mineral oil-based ferrofluid (See Supplier Information)

Strong magnet (cow magnet, bar magnet, or rare earth magnet)

Petri dish

ANSWERS TO THE FOLLOW-UP QUESTIONS

1. What factors would affect the distance observed in (b)?

   Student responses will vary, but should include: the strength of the magnet, the magnetic strength of the fluid, and the orientation of the magnet as it approaches the dish.

2. For any given spike in the final pattern observed in (c), how many nearest neighbors does it have? Why do you think this particular pattern forms?

   The pattern of spikes is formed as the fluid is dispersed along the field lines of the magnet. In doing so, the magnetite particles behave like iron filings would in the presence of a similar field. There often will be six nearest neighbors if the magnet is strong enough, and this arrangement represents a close-packed arrangement. The spikes are a reflection of the fact that the system tries to lower its energy in this way in the presence of the magnet.
3. How do you explain the behavior of the penny? How would this behavior be different if the penny were magnetic?

The formation of the spikes along the magnetic field lines forces the penny up and out of the fluid, giving it buoyancy. If the penny were magnetic, its attraction for the magnet would prevent it from being forced upward.
INVESTIGATION 1

PURPOSE

In this investigation you will experiment further with the magnetic properties of ferrofluids. More specifically, you will determine if any relationship exists between the “spiking phenomena” and the strength of the magnet used and the distance between the magnet and the fluid. In addition, you will observe the behavior of non-magnetic materials in contact with the fluid and in the field of a strong magnet.

PROCEDURE

a. Pour enough ferrofluid into a Petri dish to just cover the bottom of the dish. **CAUTION!** Ferrofluids cause stains that are difficult to remove from skin and fabrics.

b. Slowly bring one end of a strong magnet up to the fluid from **below** the dish. Note the distance from the dish to the magnet when the first spike appears. Repeat using the other end of the magnet. **It is practically impossible to remove the ferrofluid from a strong magnet so avoid direct contact of the ferrofluid with the magnet.**

c. Continue to move the magnet closer to the bottom of the dish, until it touches the dish, and note the pattern of spikes produced.

d. Hold the magnet horizontally and slowly bring it up **underneath** the dish. Note the pattern of spikes.

e. Place a penny in a Petri dish containing water. What happened to the penny?

f. Bring the magnet up **underneath** the dish. What happened to the dish? What happened to the Penny?

g. Repeat (e) and (f) above using the ferrofluid instead of water.

FOLLOW-UP QUESTIONS

1. What factors would affect the distance observed in (b)?
2. For any given spike in the final pattern observed in (c), how many nearest neighbors does it have? Why do you think this particular pattern forms?

3. How do you explain the behavior of the penny in (f)? How would this behavior be different if the penny were magnetic?
PURPOSE

To have students become familiar with the structure of magnetite and based upon this structure to determine the empirical formula for the compound. It is also possible to discuss why this substance is magnetic from these structural considerations, but this involves a discussion of octahedral and tetrahedral holes. Noting that the iron ions are occupying different types of holes in the oxide ion structure that are not chemically equivalent is worthwhile.

METHOD

The students are provided with a model of the conventional cubic unit cell and asked to construct a model of the tetragonal unit cell that is considerably easier to build. Both models can be constructed using the ICE Solid State Model Kit, but it should be noted that the cubic cell requires three (3) kits and the tetragonal model two (2) kits in order to obtain the necessary number of larger oxide spheres. Construction directions are included in the Appendix for this module. Appendix A in the Memory Metal Module of this manual contains a detailed discussion of unit cells. Be sure to emphasize that some atoms in a structure are shared by more than one unit cell and the fraction belonging to a given cell must be determined.

ANSWERS TO THE FOLLOW-UP QUESTIONS

1. For each of the structures complete the table below, indicating HOW MANY COLORLESS SPHERES LIE WITH THEIR CENTERS AT THE ___________ OF THE UNIT CELL.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
<td>8</td>
<td>12</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td>8</td>
<td>12</td>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>
2. For each of the structures complete the table below, indicating HOW MANY PINK SPHERES LIE WITH THEIR CENTERS AT THE _______________ OF THE UNIT CELL.

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<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

3. For each of the structures complete the table below, indicating HOW MANY BLUE AND RED SPHERES LIE WITH THEIR CENTERS AT THE _______________ OF THE UNIT CELL.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
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<td>12</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td>0</td>
<td>4</td>
<td>8</td>
<td>3</td>
</tr>
</tbody>
</table>

4. Convince yourself that each of the corner atoms is shared with seven other unit cells; that the edge atoms are shared with three other unit cells; and that the face atoms are shared with one other unit cell. Remember that these structures extend in all three dimensions indefinitely. It may be helpful to stack books or CD cases together to help to visualize the relationships stated above. Given that the stated information is correct, then only part of the spheres occupying each site belong to the unit cell under consideration, i.e., only 1/8 of the corner spheres, 1/4 of the edge spheres, and 1/2 of the face spheres belong to a given unit cell. Those spheres lying totally inside the cell of course belong only to that cell. Using the information above, complete the tables below.

<table>
<thead>
<tr>
<th>COLORLESS</th>
<th>CUBIC UNIT CELL (A)</th>
<th>TETRAGONAL UNIT CELL (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>__CORNERS X 1/8 =</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>__EDGES X 1/4 =</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td>PINK</td>
<td>CUBIC UNIT CELL (A)</td>
<td>TETRAGONAL UNIT CELL (B)</td>
</tr>
<tr>
<td>------</td>
<td>---------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>__CORNERS X 1/8 =</td>
<td>0</td>
<td>0</td>
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<tr>
<td>__EDGES X 1/4 =</td>
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<td>0</td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
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<td>2</td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
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<td>2</td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
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<td>4</td>
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<table>
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<th>TETRAGONAL UNIT CELL (B)</th>
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<tbody>
<tr>
<td>__CORNERS X 1/8 =</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>__EDGES X 1/4 =</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
<td>16</td>
<td>8</td>
</tr>
</tbody>
</table>

5. The ratio between the sum of the Fe (II) and Fe (III) relative to the O$^-2$ from the tables above is then:

   a. For the cubic unit cell Fe$_{24}$ O$_{32}$ And the simplest ratio is Fe$_3$ O$_4$.

   b. For the tetragonal cell Fe$_{12}$ O$_{16}$ And the simplest ratio is Fe$_3$ O$_4$. 


INVESTIGATION 2

PURPOSE

To construct a unit cell of the extended three-dimensional crystalline structure of magnetite (Fe$_3$O$_4$) and to verify this empirical formula based on this structure.

INTRODUCTION

The crystalline structure of magnetite consists of a repeating arrangement of oxide ions in what is referred to as cubic close-packed (recall the pattern of spikes that you observed in Investigation 1). Fe(II) and Fe(III) ions are distributed into some of the spaces (holes) that are created between the oxide ions. These holes do not provide the same chemical environment for all the iron ions and it is this difference in environment that results in the magnetic properties of the compound.

PROCEDURE

Following the directions as provided by your instructor, use the Solid State Model Kit to construct the layer sequences for:

- Team A: the conventional cubic unit cell.
- Team B: the tetragonal unit cell.

Alternatively your instructor may provide you with a completed model of one or both of these unit cells.

FOLLOW-UP QUESTIONS

1. For each of the structures complete the table below, indicating HOW MANY COLORLESS SPHERES LIE WITH THEIR CENTERS AT THE ______________OF THE UNIT CELL.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. For each of the structures complete the table below, indicating HOW MANY PINK SPHERES LIE WITH THEIR CENTERS AT THE _______________ OF THE UNIT CELL.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. For each of the structures complete the table below, indicating HOW MANY BLUE AND RED SPHERES LIE WITH THEIR CENTERS AT THE _______________ OF THE UNIT CELL.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>CORNERS</th>
<th>EDGES</th>
<th>FACES</th>
<th>INSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC UNIT CELL (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TETRAGONAL UNIT CELL (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that the colorless spheres are oxides, small pink spheres are ferric ions in tetrahedral holes, and blue and red are ferrous and ferric ions in octahedral holes.

4. Convince yourself that each of the corner atoms is shared with seven other unit cells; that the edge atoms are shared with three other unit cells; and that the face atoms are shared with one other unit cell. Remember that these structures extend in all three dimensions indefinitely. It may be helpful to stack books or CD cases together to help to visualize the relationships stated above. Given that the stated information is correct, then only part of the spheres occupying each site belong to the unit cell under consideration, i.e., only 1/8 of the corner spheres, 1/4 of the edge spheres, and 1/2 of the face spheres belong to a given unit cell. Those spheres lying totally inside the cell of course belong only to that cell. Using the information above, complete the tables below.
5. The ratio between the sum of the Fe (II) and Fe (III) relative to the $O^{2-}$ from the tables above is then:

   a. For the cubic unit cell Fe\_\_O\_. And the simplest ratio is Fe\_\_O\_.

   b. For the tetragonal cell Fe\_\_O\_. And the simplest ratio is Fe\_\_O\_.

<table>
<thead>
<tr>
<th>COLORLESS</th>
<th>CUBIC UNIT CELL (A)</th>
<th>TETRAGONAL UNIT CELL (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>__CORNERS X 1/8 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__EDGES X 1/4 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PINK</th>
<th>CUBIC UNIT CELL (A)</th>
<th>TETRAGONAL UNIT CELL (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>__CORNERS X 1/8 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__EDGES X 1/4 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RED AND BLUE</th>
<th>CUBIC UNIT CELL (A)</th>
<th>TETRAGONAL UNIT CELL (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>__CORNERS X 1/8 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__EDGES X 1/4 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__FACES X 1/2 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__INSIDE X 1 =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>__TOTAL IN CELL =</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXPERIMENT 1
Notes for the Instructor

PURPOSE

To synthesize magnetite nanoparticles in aqueous solution using a variety of FeCl₂ to FeCl₃ mole ratios. Once prepared, the nanoscale particles are coated with the surfactant tetramethylammonium hydroxide to create a ferrofluid whose appearance is altered reversibly by the presence of a strong magnetic field. The “spikes” that appear in the presence of the magnet can be used as a rough measure of the success of the synthesis and as a means for estimating the stoichiometry of the reaction.

METHOD

The students follow a general procedure for the production of aqueous-based ferrofluids with the exception that they will use various ferrous-to-ferric mole ratios in the synthesis. Students will then decide which of the resulting fluids produces spikes similar to those they observed in Investigation 1 and thereby estimate the correct stoichiometric ratio for the reactants.

A pre-lab discussion could include a discussion of nanoparticles and surfactants. For the surfactant employed in this experiment, tetramethylammonium hydroxide, a reasonable expectation is that the hydroxide anions could bind to iron atoms at the surface of the magnetic nanoparticles and tetramethylammonium cations could form a sheath around the negatively-charged particles through electrostatic attraction. These sheaths of positive charge can prevent the particles from agglomerating. The magnetic properties of the magnetite particles are also noteworthy but the level of discussion needs to reflect student familiarity with electron configurations. If the main focus of the experiment is on stoichiometry, discussions of electron spins can be deferred and revisited later in the course. See Appendix A or the background information for this module for a more complete discussion of this topic.

MATERIALS

- Magnetic stirrers and stir bars
- Cow magnets (0.5 in. x 3 in.), available from farm supply stores or from Edmund Scientific, Barrington, NJ.
- Strong magnet (neodymium-iron-boron), available from the physics department or Edmund Scientific. Computer hard drive magnets will also work.
- 2.0 M FeCl₂ in 2 M HCl
- 1.0 M FeCl₃ in 2 M HCl
- 0.7 M NH₃
- 25% aqueous tetramethylammonium hydroxide solution, available from Aldich, Milwaukee, WI.
ANSWERS TO ANALYZING THE DATA

1. Determine the mole ratio of FeCl$_3$ to FeCl$_2$ and enter in the table below. Show your work!

<table>
<thead>
<tr>
<th>GROUP</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>RATIO</td>
<td>0.5:1</td>
<td>1:1</td>
<td>1.5:1</td>
<td>2:1</td>
<td>2.5:1</td>
<td>3:1</td>
<td>3.5:1</td>
</tr>
</tbody>
</table>

2. Which of the ratios from the table above corresponds to the fluids that produced the best spiking behavior?

   Students should find that stoichiometric ratios from 1.5:1 to 2.2:1 yield spikes, but outside these parameters little or no spiking occurs. The best results, however, are observed with a 2:1 ratio.

3. Use your answer to question (2) above to balance the equation for the synthesis reaction below.

   \[
   \underline{2} \text{FeCl}_3 + \underline{1} \text{FeCl}_2 + \underline{8} \text{NH}_3 + \underline{4} \text{H}_2 \text{O} \rightarrow \underline{1} \text{Fe}_3 \text{O}_4 + \underline{8} \text{NH}_4 \text{Cl}
   \]
EXPERIMENT 1

PURPOSE

To determine experimentally the optimum mole ratio between FeCl₂ and FeCl₃ reactants used in the synthesis of a so-called “ferrofluid” whose appearance is altered by the presence of a magnet.

INTRODUCTION

The successful synthesis of a ferrofluid begins with the formation of a colloidal suspension of magnetic nanoparticles in a liquid medium. These colloids are suspensions of very small particles on the order of 100 nanometers (10nm) in size. By synthesizing the nanoparticles in the presence of molecules called surfactants, the particles can be suspended in solution rather than clumped together.

These ferrofluids possess the interesting property of “spiking” that you observed in Investigation 1. This spiking will be used to determine whether a high-quality ferrofluid has been produced, conversely, the formation of a high-quality ferrofluid will be used to optimize the synthesis and to estimate the stoichiometric ratio needed for complete reaction of the two iron solutions used in the synthesis.

You and your partner will make an aqueous-based ferrofluid following the procedure below. Your instructor will assign to you a specific combination of the FeCl₂ and FeCl₃ solutions and your results will be pooled with those from your classmates.

SAFETY PRECAUTIONS

All of the chemicals used in this synthesis are to be handled with extreme caution. Remember that ferrofluids can be messy and this particular one will permanently stain almost any fabric. Do not let the fluid come into contact with any magnet. Keep the magnet and the ferrofluid well separated at all times.

PROCEDURE

1. To a 100 mL beaker add the amounts of the stock 2M FeCl₂ and stock 1M FeCl₃ solutions assigned to you by your instructor. Add a magnetic stirring bar and begin stirring. Use a buret to add 50 mL of 0.7M aqueous ammonia (NH₃) drop by drop to the solution. A black precipitate of magnetite should form as you slowly add the ammonia solution over a period of about 5 minutes.
2. Turn off the stirrer and quickly use a strong magnet to slide the stir bar up the walls of the beaker. Remove the stir bar with gloved hands before it touches the magnet.

3. Let the magnetite settle for a few minutes, then decant and discard the clear liquid, making sure to save as much of the solid as possible. Transfer the solid to a plastic weighing boat. It may be necessary to rinse the beaker with water from a wash bottle.

4. Use a strong magnet to hold the magnetite to the bottom of the weighing boat and once again decant as much of the clear liquid as possible. Repeat this step two more times.

5. Add 2.0 mL of 25% tetramethylammonium hydroxide and stir with a glass stir rod to suspend the solid in the liquid. Using the strong magnet to hold the ferrofluid to the bottom of the weighing boat, pour off and discard the liquid. Move the magnet around and pour off the remaining liquid.

6. Place a cow magnet or other very strong magnet under the remaining fluid and record your observations relative to its spiking behavior. If the fluid does not spike readily, then add one drop of water and try again. Share your ferrofluid results with the rest of the class and be sure to observe the spiking behavior of the ferrofluids produced by your classmates.

### DATA TABLE I

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL 1 M FeCl₃</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>mL 2 M FeCl₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>“spiking” (Y or N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### ANALYZING THE DATA

1. Determine the mole ratio of FeCl₃ to FeCl₂ and enter in the table below. Show your work!

<table>
<thead>
<tr>
<th>GROUP</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>RATIO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Which of the ratios from the table above corresponds to the ferrofluids that produced the best spiking behavior?

3. Use your answer to question (2) above to balance the equation for the synthetic reaction below.

\[ \text{___FeCl}_3 + \text{___FeCl}_2 + \text{___NH}_3 + \text{___H}_2 \text{O} \rightarrow \text{___Fe}_3 \text{O}_4 + \text{___NH}_4 \text{Cl} \]
Ferrofluid Review Questions

1. Elemental iron is ferromagnetic, yet an iron nail does not attract iron filings.
   a. Explain.

   In the absence of an external magnetic field, the magnetic domains of iron are randomly oriented; thus, there insufficient net magnetization for attraction to occur.

   b. If, however, a magnet is rubbed over the surface of a nail, the nail will attract iron fillings. Why?

   The magnet aligns or orients the domains with the applied external field, creating a larger net magnetization in the nail.

2. Analysis of a compound shows it to be potassium, 49.4%; sulfur, 20.2%; and oxygen, 30.4%. What is its empirical formula?

   Assume 100 g so 49.4% = 49.4g, 20.2% = 20.2g, 30.4% = 30.4g

   Potassium = 39.1 g/mol ----- \( \frac{49.4 \text{ g}}{39.1 \text{ g/mol}} = 1.26 \text{ mol} \)

   Sulfur = 32.1 g/mol ----- \( \frac{20.2 \text{ g}}{32.1 \text{ g/mol}} = 0.629 \text{ mol} \)

   Oxygen = 16.0 g/mol ----- \( \frac{30.4 \text{ g}}{16.0 \text{ g/mol}} = 1.9 \text{ mol} \)

   Divide each number of moles by the smallest amount of moles.

   \( \frac{1.26 \text{ mol K}}{0.629 \text{ mol}} \sim 2 \quad \frac{0.629 \text{ mol S}}{0.629 \text{ mol}} \sim 1 \quad \frac{1.9 \text{ mol O}}{0.629 \text{ mol}} \sim 3 \)

   Therefore, the empirical formula is \( \text{K}_2\text{SO}_3 \).
3. Consider the layered structures below and determine the total number of each type of atom belonging to the unit cell and the empirical formulas for the compound.
Use the data from the tables above.

a. What is the total number of each type of atom in the unit cell?  K __4__  
Pt __2__;  Cl __12__

b. What is the empirical formula for this compound? _____ K2PtCl6 _____

4. Determine the mole ratios from the balanced equation below.

\[3 \text{ CuO} + 2 \text{ NH}_3 \rightarrow 3 \text{ Cu} + \text{ N}_2 + 3 \text{ H}_2\text{O}\]

\[\text{CuO} : \text{Cu} \quad \text{NH}_3 : \text{CuO} \quad \text{N}_2 : \text{NH}_3 \quad \text{Cu} : \text{H}_2\text{O}\]

\[3 : 3 \text{ or } 1 : 1 \quad 2 : 3 \quad 1 : 2 \quad 3 : 3 \text{ or } 1 : 1\]
5. Compare the solids VO and V$_2$O$_5$ in their attraction to a magnetic field.

*Note: This question requires knowledge of electron configurations and oxidation states*

Vanadium in VO has a formal oxidation state of +2 and an odd number of electrons (3), making it paramagnetic. In contrast, V$_2$O$_5$ has a formal oxidation state of +5 and no unpaired electrons, making it diamagnetic. Thus, VO is more strongly attracted to a magnetic field.
Ferrofluid Review Questions

Name __________________
Date ________  Hour _____

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

2. Analysis of a compound shows it to be potassium, 49.4%; sulfur, 20.2%; and oxygen, 30.4%. What is its empirical formula?
3. Consider the layered structures below and determine the total number of each type of atom belonging to the unit cell and empirical formulas for the compound.
<table>
<thead>
<tr>
<th>Potassium Atoms</th>
<th>Sites in the Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Edges</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Faces</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inside</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>Total in Cell</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Platinum Atoms</th>
<th>Sites in the Unit Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Edges</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Faces</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inside</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>Total in Cell</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chloride Atoms</th>
<th>Sites in the Unit Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Edges</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Faces</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inside</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>Total in Cell</td>
<td></td>
</tr>
</tbody>
</table>

Use the data from the tables above.

a. What is the total number of each type of atom in the unit cell?  
   K ____; Pt ____; Cl ____.

b. What is the empirical formula for this compound? ________________

4. Determine the mole ratios from the balanced equation below.

   \[ 3 \text{CuO} + 2 \text{NH}_3 \rightarrow 3 \text{Cu} + \text{N}_2 + 3 \text{H}_2\text{O} \]

\[
\begin{align*}
\text{CuO} : \text{Cu} & \quad \text{NH}_3 : \text{CuO} & \quad \text{N}_2 : \text{NH}_3 & \quad \text{Cu} : \text{H}_2\text{O}
\end{align*}
\]
5. Compare the solids VO and V$_2$O$_5$ in their attraction to a magnetic field.
Ferrofluid Assessment

Name ___________________

Date _________  Hour  _____

Matching

Match the word with the best definition.

__E__  1. stoichiometry    a. weak forces of attraction between molecules
__D__  2. spikes            b. a 3-D parallelepiped that, when shifted along each edge
__H__  3. ferromagnetism   by the length of the edge creates the entire structure of
__F__  4. colloid           atoms in a crystal
__I__  5. hole              c. regions where unpaired electrons strongly interact with
__G__  6. ferrimagnetism    one another and align, even in the absence of a
__C__  7. magnetic domain   magnetic field
d. a pattern of uplifted suspended particles that results
   from placing a magnet near a ferrofluid
__B__  8. Unit cell         e. a word describing that part of chemistry that deals with
__J__  9. Nanoparticle      the relative amounts of substances involved in chemical
__L__ 10. empirical formula f. a dispersion of particles from ~ 1 nm to 1000 nm
__M__ 11. surfactant        g. a phenomenon in which the internal magnetic moments
__N__ 12. ferrofluid        of multiple spin sets of unpaired electrons within the
__K__ 13. magnetite         magnetite domain of a solid partially cancel and thus
__A__ 14. Van der Waals forces leave a net spin

h. a phenomenon in which the internal magnetic moments
   of unpaired electrons within a domain of the solid are
   aligned and act cooperatively
i. an empty site in a crystalline solid
j. a very small particle on a scale of nanometers (10⁻⁹ m)
k. the name for Fe₃O₄
l. information that gives the simplest ratio between the
   atoms of the elements present in a compound
m. a molecule that surrounds particles and isolates them
   from the attractive forces of their neighbors
n. a suspension of a magnetic solid in a liquid that
   responds to an external magnetic field
Multiple Choice
Choose the best answer.

__A__ 15. Ferrofluids exhibit magnetic properties because
   a. they consist of a magnetic solid suspended in a liquid medium.
   b. they become magnetic under the influence of the earth's magnetic field.
   c. they consist of positively and negatively charged ions.
   d. none of the above.

__D__ 16. The potential advantage of using a ferrofluid to administer medication is
   a. that it is cheaper.
   b. that it also acts as an iron supplement.
   c. that it tastes better.
   d. that it can be directed to specific sites in the body.

__B__ 17. In the production of a ferrofluid, the van der Waals attractions can be overcome by
   a. shielding the reaction vessel from the earth's magnetic field.
   b. adding a substance called a surfactant.
   c. adding a substance called a catalyst.
   d. adding a coagulating agent.

Problems

18. a. Not all of the atoms occupying each site in a unit cell belong to that unit cell. What fraction of each of the following belong to a given unit cell?

<table>
<thead>
<tr>
<th>Edge</th>
<th>1/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face</td>
<td>1/2</td>
</tr>
<tr>
<td>Corner</td>
<td>1/8</td>
</tr>
<tr>
<td>Inside</td>
<td>1</td>
</tr>
</tbody>
</table>

b. Based on your answers in part a, sodium thallide was constructed and contained the following

<table>
<thead>
<tr>
<th>Sodium Atoms</th>
<th>Sites in the Unit Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Corners</td>
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</tr>
<tr>
<td>0</td>
<td>Edges</td>
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</tr>
<tr>
<td>4</td>
<td>Faces</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Inside</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Total in Cell</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thallium Atoms</th>
<th>Sites in the Unit Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
</tr>
</thead>
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</table>

c. What is the total number of each type of atom in this compound?  Na$_7$Tl$_7$
d. What is the empirical formula for this compound? ______NaTl_______

19. Determine the percent composition of each element in magnetite.

Oxygen = 16.0 g/mol  -----  4 x 16.0 g/mol = 64.0 g/mol

Iron = 55.8 g/mol  -----  3 x 55.8 g/mol = 167.4 g/mol

Total compound formula weight = 231.4 g/mol

Percent oxygen by mass = (64.0 / 231.4) x 100 = 27.7%

Percent iron by mass = (167.4 / 231.4) x 100 = 72.3%

20. The mole ratio of NH$_4$OH to NH$_4$Cl was experimentally determined to be 4 : 2; balance the equation below.

$\underline{1}$ MnCl$_2$ + $\underline{1}$ Br$_2$ + $\underline{4}$ NH$_4$OH → $\underline{4}$ MnO$_2$ + $\underline{2}$ NH$_4$Cl + $\underline{2}$ NH$_4$Br + $\underline{2}$ H$_2$O
Ferrofluid Assessment

Name ___________________  
Date _________  Hour  _____

Matching
Match the word with the best definition.

____ 1. stoichiometry  
a. weak forces of attraction between molecules
____ 2. spikes  
b. a 3-D parallelepiped that, when shifted along each edge by the length of the edge creates the entire structure of atoms in a crystal
____ 3. ferromagnetism  
c. regions where unpaired electrons strongly interact with one another and align, even in the absence of a magnetic field
____ 4. colloid  
d. a pattern of uplifted suspended particles that results from placing a magnet near a ferrofluid
____ 5. hole  
e. a word describing that part of chemistry that deals with the relative amounts of substances involved in chemical reactions
____ 6. ferrimagnetism  
f. a dispersion of particles from ~ 1 nm to 1000 nm
____ 7. magnetic domain  
g. a phenomenon in which the internal magnetic moments of multiple spin sets of unpaired electrons within the magnetite domain of a solid partially cancel and thus leave a net spin
____ 8. Unit cell  
h. a phenomenon in which the internal magnetic moments of unpaired electrons within a domain of the solid are aligned and act cooperatively
____ 9. Nanoparticle  
i. an empty site in a crystalline solid
____ 10. empirical formula  
j. a very small particle on a scale of nanometers (10⁻⁹ m)
____ 11. surfactant  
k. the name for Fe₃O₄
____ 12. ferrofluid  
l. information that gives the simplest ratio between the atoms of the elements present in a compound
____ 13. magnetite  
m. a molecule that surrounds particles and isolates them from the attractive forces of their neighbors
____ 14. Van der Waals forces  
n. a suspension of a magnetic solid in a liquid that responds to an external magnetic field
Multiple Choice
Choose the best answer.

15. Ferrofluids exhibit magnetic properties because
   a. they consist of a magnetic solid suspended in a liquid medium.
   b. they become magnetic under the influence of the earth's magnetic field.
   c. they consist of positively and negatively charged ions.
   d. none of the above.

16. The potential advantage of using a ferrofluid to administer medication is
   a. that it is cheaper.
   b. that it also acts as an iron supplement.
   c. that it tastes better.
   d. that it can be directed to specific sites in the body.

17. In the production of a ferrofluid, the van der Waals attractions can be overcome by
   a. shielding the reaction vessel from the earth's magnetic field.
   b. adding a substance called a surfactant.
   c. adding a substance called a catalyst.
   d. adding a coagulating agent.

Problems

18. a. Not all of the atoms occupying each site in a unit cell belong to that unit cell. What fraction of each of the following belong to a given unit cell?

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<th>Face</th>
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<tbody>
<tr>
<td>Corner</td>
<td>Inside</td>
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b. Based on your answers in part a, sodium thallide was constructed and contained the following:

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<th>Sodium Atoms</th>
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</table>

<table>
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<th>Thallium Atoms</th>
<th>Sites in the Unit Cell</th>
<th>Atoms in the Unit Cell From that Site</th>
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</table>

c. What is the total number of each type of atom in this compound? ______________
d. What is the empirical formula for this compound? ______________

19. Determine the percent composition of each element in magnetite.

20. The mole ratio of NH₄OH to NH₄Cl was experimentally determined to be 4 : 2; balance the equation below.

  _____ MnCl₂ + _____ Br₂ + _____ NH₄OH → _____ MnO₂ + _____ NH₄Cl + _____ NH₄Br + _____ H₂O
The magnetic properties of magnetite can be explained in terms of its crystalline structure. As was seen in Investigation 2, magnetite crystallizes in an inverse spinel structure within which the oxide ions are arranged in a cubic close-packed structure. Within this arrangement iron (II) ions occupy 1/4 of the octahedral holes (holes that are formed by six oxide ions in the shape of an octahedron). There are twice as many iron (III) ions as iron(II) ions, and the trivalent ions are equally divided between 1/8 of the tetrahedral holes (holes formed by four oxide ions in the geometry of a tetrahedron) and 1/4 of the octahedral holes.

Iron (III) has a $d^5$ electronic configuration and five unpaired electrons. The spins of the iron (III) ions in octahedral and tetrahedral holes are antiparallel and no net magnetization results from these ions. The iron (II) ions have a $d^6$ electronic configuration with four unpaired electrons and are responsible for the net magnetization. These divalent ions tend to align their spins parallel to those of the iron (III) ions in adjacent octahedral holes.

The magnetite nanoparticles represent a single magnetic domain and as such are described as superparamagnetic. In a sample of magnetite, there are many magnetic domains as represented below. Within a given domain the electron spins are pointed in a common direction, but the directions can change from one domain to another.

Introduction of a magnetic field $H$ can align the spins in all domains in the direction of the field as indicated above. This results in a substantial magnetization of the suspended solid, which, in turn, gives the entire fluid a net magnetization. Under the influence of the field, what are normally small waves on the surface of the fluid caused by the thermodynamic and hydrodynamic properties of the colloidal suspension, become amplified until the waves become peaks or spikes. When the field is removed, the magnetic domains of the particles become randomly orientated relative to one another due to thermal agitation.