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Section I:

A Brief History of Chemistry— Independent Research Copics

Mixing Metals to Make Bronze

Fronze was one of the earliest alloys to be made and used. Which elements have been used to make bronzes? What different methods have been used for the manufacture of bronze artifacts by different cultures over the years?

Bronze is an alloy made from about 90 percent copper, which is mixed with other metals in the liquid phase to form a homogenous solution and then is solidified to a single solid alloy. Before 3000 B.C., it was discovered that melting copper from some ores gave rise to a substance that melted easily, could be poured into a mold, and was a tougher and harder material that could make better weapons. This copper ore contained arsenic, and so the first bronze was formed. Later, tin became an essential metal that was included with the copper and arsenic. Smaller amounts of antimony and lead are also found in many bronzes. Geology professor Dr. Richard Cowen writes the following description of the Bronze Age:

In time, a skilled smith would be able to have some control over the end product, producing not copper, not a random unknown alloy, but a specific alloy to suit the job at hand. The Bronze Age marks the time at which smiths became metallurgists, makers of magic, heroes, and gods. Bronze Age smiths were often buried with the tools of their trade: hammers, an anvil, knives and molds.

All methods used for the manufacture of bronze artifacts began with molten metal. This molten metal could be poured into an open stone mold ("open casting"), and, when cool, the object would be hammered into a final shape using traditional "smithing" techniques and could also be honed with a flint to obtain a sharp edge if that was desired. Later, molds of stone or ceramic were made in two pieces that could be separated to release the final cast object.

About a thousand years later, the "lost-wax" method was invented. Using this method, a wax model of the desired

casting shape would be made. Pottery clay would then be formed around the wax model, and then the whole model would be placed in a furnace. The wax would melt and would then be poured away, leaving a precisely shaped cast into which molten metal would be poured.

For larger art objects, a ceramic "core" might be formed, with the wax added and then more clay around that. When the wax was removed and the bronze poured in, the metal would form a thin shell around the ceramic core. This method saved money because it did not require as much expensive metal. A very similar method is used today.²

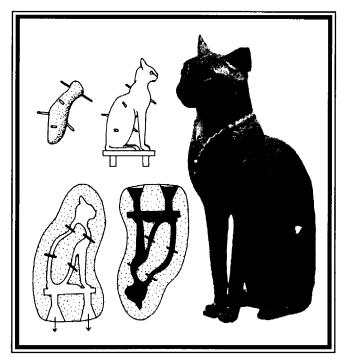


Diagram showing the stages by which Egyptian foundrymen cast a bronze statuette of a cat, c. 1500 B.C.

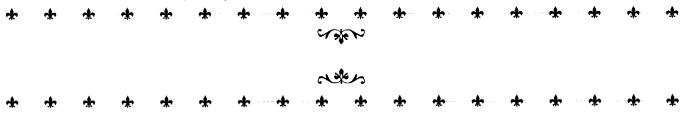


Dr. Cowen describes Chinese sophistication in bronze work thusly:

The Chinese became more sophisticated bronze metallurgists than their Western counterparts. The famous terracotta army of the Emperor Qin, made for him about 220 B.C. and buried with him, have weapons that are basically bronze, but they have been deliberately alloyed with metals such as titanium, magnesium, cobalt, and so on, no doubt after empirical trial and

error, to give superior hardness and penetrating power. This weaponry, combined with technological advances such as fast-loading crossbows, united China under the Oin dynasty and defended it against invaders.

Bronzes approximately one thousand years old from Ife and Benin in Africa indicate that the lost-wax casting technology had reached a high level of accuracy at that point in history.⁴



The Use of Dye and Preservatives

independent research, you should find out how colors were extracted and used in the form of dyes, such as "Tyrian purple," and preservatives. In what ways were dyes and preservatives used to assist mummification, reform textiles, and used in artworks?

Substances exhibiting color intrigued humans from an early date. Cave paintings in brilliant reds and blacks dating back tens of thousands of years have been found in the Pyrenees region of southern France. Egyptian tombs from early dynasties are painted in brilliant colors. Many textiles surviving from early times still have colors made from plants such as woad and later from indigo, another plant extract. Ten thousand years ago, woad seeds that could yield a blue dye were being harvested and transported across Europe and elsewhere, so linen and hemp could be dyed blue with woad.

Such materials have been found in a variety of locations, including ancient Egypt.⁵ Mummy wrappings were dyed with various colors including woad. In the mummification process, preservatives made from red or yellow oxides of mercury were used to color cloth and skin, and they were

also used as preservatives since they killed or inhibited bacteria that caused decay. These and many other pigments have been found in prepared form in jars and in tombs, and recipes for their manufacture are described on ancient papyri. From the time of the Egyptian pharaohs through the Roman Empire and peaking in activity in the Middle Ages, craftsmen colored glass in brilliant hues by adding chemical oxides to the molten glass. Such glass was widely used in church windows across Europe, providing a highly colorful augmentation to religious motifs.

Tyrian purple, also known as royal purple, was a brilliant purple dye extruded from the shells of sea snails found in the Mediterranean Sea near the city of Tyre. The extrusion used to create this dye starts as a clearer liquid, but turns dark in sunlight. It was rare, and thus costly, and became a symbol of wealth and opulence. Other species of snails, including ones in the Caribbean, have also produced blue colors. The ancient Phoenicians developed a major industry around the production of this dye and the cloth dyed with it. This royal purple dye was probably produced even earlier in Minoan Crete. Its chemical composition was finally determined in 1909, and it was found to be a close relative of a compound called "indigo," which is a well established blue pigment that is still widely used today.



Alchemy and the Philosopher's Stone

In your independent research, you should discover why chemistry entered a period that focused on a discipline known as "alche-

my." A popular substance sought by alchemists was the "philosopher's stone." What was the "philosopher's stone"?

The use of "chemistry" as a term is credited to an edict of Emperor Diocletian in 296 A.D., and this document seems to refer to Egypt as the place where chemistry had its origins. The *Leyden Papyrus*, written around 300 A.D. in Egypt, has a collection of recipes for fraudulent "transmutations" of cheap materials into precious metals, valuable dyes, or gemstones." Alexandria had the earliest known books on chemistry. Because of the involvement of the Arab world in early efforts at chemistry, early historical writers added the definite article "al" before "chemeia" to get "alchemy." This term came to refer to a practice in which practical chemistry, astrological ideas, and religion were combined to form a "new science."

Early efforts to describe color changes that resulted from chemical reactions gave way to persistent attempts to change base metals into gold or silver. Since heating lead or mercury in air gave rise to yellow- or red-colored oxides, and heating copper with arsenic gave rise to a white powder that resembled silver, alchemists believed that a single substance, the so-called "philosopher's stone," possessed the power to effect such changes. No such single substance was ever found, though many false claims were made.

The work done by early Greek scientists went unnoticed until the Arab conquest of Egypt in 640 A.D. Works on the topic of alchemy were translated into Arabic and then Latin, and by the year 1000 A.D., the practice of alchemy had become widespread. Separately, it seems, similar ideas were prevalent in Chinese and Indian cultures. Later, alchemy became an instrument of fraud, as wandering alchemists sought out wealthy patrons who would buy their services to transmute metals. Roger Bacon (1214–92 A.D.), an English philosopher working at Oxford University, wrote about alchemy and began to identify the difference between the practical aspects of chemistry and attempted frauds. Bacon was possibly the first person to promote chemistry as an important contributor to medicine and as an intermediate field between physics and biology.



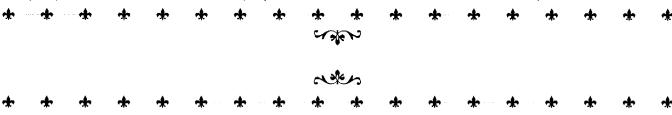
Gunpowder and Fireworks

In your independent research, you should find out where gunpowder and fireworks were invented. For what purposes were gunpowder and fireworks used when these inventions became more widely known?

Gunpowder is a mixture of potassium nitrate (saltpeter), charcoal, and sulfur, and it is believed to have been discovered by the Chinese sometime before 1100 A.D. Roger Bacon included a recipe for gunpowder in his work titled *Opus tertium*, which he sent to the Pope in 1268 A.D., so we know that information about gunpowder had reached Europe by that time. The Chinese used gunpowder for

rockets and explosive projectiles that could be thrown using catapults. "By the 1200s, a Chinese Bureau of Munitions was operating seven factories that produced 7,000 rockets and 21,000 bombs a day."?

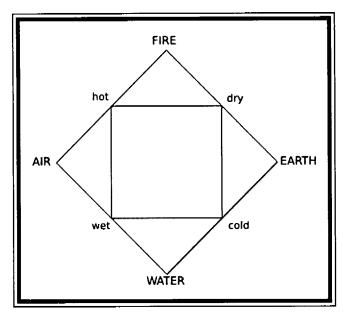
Eventually, cannons were invented to provide more firepower. Europe and Arabia rapidly realized the military potential of gunpowder. At the battle of Crecy in 1346 A.D., the English arsenal included some gunpowder, but it was only in the next century that weaponry using gunpowder began to dominate. Subsequently, the firepower became so great that the idea of building stone fortified towns and castles as defense structures slowly became obsolete.



Early Thinkers on the Nature of Matter

The famous Greek philosophers Aristotle and Democritus thought deeply about the world in which they lived. How did these philosophers explain the nature of matter?

Ancient Greek philosophers were strongly influenced by the ideas of geometry introduced by Euclid. Aristotle (384–322 B.C.) brought together ideas from earlier philosophers, including Plato (427–347 B.C.), who was the first to use the term "element" ("stoicheia" in Greek). Each element



A diagram of the four elements and four properties as envisioned by Aristotle.

C 360

was thought to have a specific three-dimensional geometric shape (e.g., cube, pyramid, prism, etc.), and the final combinations of these shapes were thought to make up the final form (e.g., crystals) observed in nature.

Aristotle posited that four specific properties—hot, cold, wet, and dry—combined to form the four elements, fire, air, water, and earth. Aristotle added a fifth "immaterial" element, which accounted for energy transmission. The idea that there existed only four material elements into which all other substances could be broken down persisted for many centuries. The fifth element became the "ether," the existence of which was finally disproven in the nineteenth century.

Democritus (460–370 B.C.), or Demokritus of Abdera, extended the idea, probably initiated by Aristotle, that large numbers of small hard discrete particles make up matter. This concept differed from earlier notions of matter as having some form of continuous structure. These particles, or atoms, were too small to be observed directly. Similar ideas were probably being introduced in India and other cultures around the same time. It is not clear who first assigned a mass to such particles, but differences in the properties of these atoms were proposed, as they were thought to differ in color, taste, and smell.



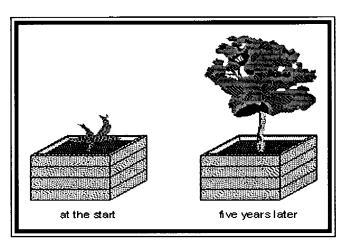
The "Living Tree" Experiment

The classic "living tree" experiment was performed by Jan Baptiste van Helmont, and others repeated his experiments. Your research should find out what these experiments involved, how early scientists interpreted their results, and what we now believe the results mean.

The famous French chemist Antoine Lavoisier (1743–94) was among those intrigued by the results of the "living tree" experiment performed by Jan Baptiste van Helmont (1580–1644). Van Helmont pondered living systems and their chemistry and questioned where the growth of trees and plants originated. Obvious answers were soil and water, but too little was understood about the atmosphere. One of van Helmont's major contributions was to establish the meaning of "gas" and identify carbon dioxide as a component of air, coming from combustion and fermentation, that had the ability to extinguish a candle.

Following is a translation of van Helmont's own description of his living tree experiment:

But I have learned by this handicraft-operation that all Vegetables do immediately, and materially proceed out of the Element of water onely. For I took



Following his "Living Tree" experiment, Van Helmont concluded that the tree's growth was a result of its water intake.



an Earthen vessel, in which I put 200 pounds of Earth that had been dried in a Furnace, which I moystened with Rainwater, and I implanted therein the Trunk or Stem of a Willow Tree, weighing five pounds; and at length, five years being finished, the Tree sprung from thence, did weigh 169 pounds, and about three ounces: But I moystened the Earthen Vessel with Rain-water, or distilled water (alwayes when there was need) and it was large, and implanted into the Earth, and least the dust that flew about should be co-mingled with the Earth, I covered the lip or mouth of the Vessel with an Iron-Plate covered with Tin, and easily passable with many holes. I computed not the weight of the leaves that fell off in the four Autumnes. At length, Lagain dried the Earth of the Vessell, and there were found the same two hundred pounds, wanting about two ounces.

Therefore 164 pounds of Wood, Barks, and Roots, arose out of water onely.8

Van Helmont believed that since the tree had gained weight, but the soil had lost very little weight, it proved that the weight gain was a result only of the tree taking in water. This experiment by van Helmont has been cited as being among the first well-documented examples of attention to scientific detail and experimental controls. However, this experiment has also been widely criticized, though there is considerable controversy regarding the criticisms. Now that we fully understand photosynthesis, we are aware that carbon dioxide from the air is a major contributor to the tree's weight, in addition to water. Small amounts of nutrients from the soil were indeed utilized, which may account for the soil's weight loss.



Antoine Lavoisier and His Role and Fate in the French Revolution

Along with his scientific efforts, what was O Antoine Lavoisier's role and fate in the French Revolution?

Antoine Lavoisier was born in 1743, the son of a wealthy avocate (lawyer) in a suburb of Paris. He died in 1794 when he was guillotined in La Place de la Revolution in Paris. Lavoisier is often called the Father of Modern Chemistry. Lavoisier's training and experience was in the realm of law, finance, and accounting, but in addition to his law degree, he also had a college education in astronomy, botany, geology, and chemistry. Lavoisier's forte was his ability to bring the skills and care of an accountant to his scientific studies. He strongly believed that everything must be accounted for, and his main instrument was the scientific balance.

In the thirty years between 1764 when he qualified as a lawyer and his death, Lavoisier occupied an incredible number of administrative positions. Some were related to science, but many were in economics and finance. Lavoisier was intensely patriotic and did not want France to be left out of the scientific revolution that was occurring at that time. He believed strongly in using science in the service of people, both the wealthy and the poor. However, Lavoisier had to tread a fine line between loyalty to the monarchy (the *ancien régime*) and service to the revolutionaries who were gaining strength in France and with whom he shared many ideals. Not surprisingly, therefore, he had both strong supporters and powerful enemies.

Lavoisier worked as an investor, tax collector, accountant, and chemical analyst for the Ferme Generale, a private company that collected taxes on behalf of the French government, and he eventually became the director of this

firm. Lavoisier was also an assistant chemist, full member, and then director of the Academie de Science (Academy of Sciences). He worked as an assistant geologist and mapping surveyor for much of France, was the founder and director of the Gunpowder and Saltpeter Commission, was a wealthy landowner and experimental agriculturist, and was also a social economist, devising and reporting on a variety of models for the future of France.

For the Academy of Sciences, Lavoisier headed committees that were charged with responding to government requests for reports on a wide variety of topics, including Parisian street lighting, Parisian water supplies, prisons, public health, theatre and theatre lighting design, air quality and health, a mineralogical atlas of France, a comparison of hot-air and hydrogen for balloon flights, the relocation of slaughterhouses in Paris, and the quality of marketed tobacco. Lavoisier became an active and enthusiastic member of a group that called themselves "physiocrats." The physiocrats aimed to develop logical systems for handling the country's finances that would more fairly reward and include all members of the community, from peasants to aristocrats.

The Ferme Generale's responsibilities included customs collections. Smuggling was a widespread problem at the time, and so in 1779 Lavoisier proposed that a wall be built around Paris to allow better customs control. This was finally undertaken at much expense in 1787. Lavoisier was deeply involved in this project, and not surprisingly this made him very unpopular. The wall and its tollgates were later burned and completely demolished, and the Ferme Generale was abolished in 1791 by the National Assembly.¹⁰



Portrait of Antoine Lavoisier, considered the father of modern chemistry.

Prior to the revolution. Lavoisier had risen to become president of *la Caisse d'Escompte* (the Discount Bank), which provided massive financial support to the French king and to the American war of independence. Lavoisier proposed fiscal reforms that would temper France's punitive tax system and would provide for a more equitable distribution of resources throughout the country. Most of his proposals

were not implemented, as divisions between those supportive of the *ancien régime* and those calling for total revolution grew. In July of 1789, these tensions eventually erupted into widespread rioting. As Director of the Gunpowder and Saltpeter Commission both before and after the storming of the Bastille on July 14, 1789, Lavoisier played a role in some of the most chaotic days in France's history. He transferred gunpowder stored at the arsenal to the Bastille on the eve of July 14 to serve the rising peoples' power. Two months later, he supervised the demolition of the Bastille.

Lavoisier sympathized with the new regime and even tried to become a Third Estate deputy to the National Assembly, although he was rejected for being a noble. He supported the idea of a constitutional monarchy, but more powerful forces that favored a republican form of government came to the fore. Lavoisier acted as a consultant to the new government on many financial and military issues. In 1793, he even spent considerable time and energy researching methods for printing the new currency notes. The metric system and decimal currency were worked out during the period from 1790 to 1793.

Although Lavoisier sympathized with the new regime, his life was to be negatively impacted by the agenda of the new government. The National Convention voted to abolish the National Academy of Sciences in August 1793. In September of that year, the Reign of Terror began. On October 17, 1793, the "Law of Suspects" was passed, and enmity toward former employees of the *Ferme Generale* boiled to the surface, and on November 24, 1793, several former employees of the *Ferme Generale* were placed under arrest.

Lavoisier hid out for several days. Then, in an effort to save himself, he claimed that he had left the *Ferme* three years earlier and was engaged in important work for the revolutionary government. Together with his father-in-law, Lavoisier surrendered on November 28. Former colleagues tried to rally support for Lavoisier's release on the basis of his patriotism and his support for the revolution, but in the end Lavoisier and twenty-seven former members of the *Ferme Generale* were convicted of conspiring to aid the enemies of France and were guillotined on May 8, 1794.



Madame Lavoisier

Yow was Madame Lavoisier involved in Oher husband's chemistry work? What was her fate during and after the French Revolution?

A recent account by organic chemist and Nobel laureate Roald Hoffmann details how Marie Anne Pierrette Paulz met Antoine Lavoisier and, following their marriage in 1771, contributed greatly to his work and publications. Madame Lavoisier's father was a leader in the *Ferme Generale*, the tax collecting company in which Lavoisier purchased a share and where he went to work. Although she was only thirteen years old at the time of their marriage, she learned about chemistry, so she could assist in the laboratory. She also learned English, so she could translate works and articles published by British chemists and physicists who were very active in this period. With a talent for art, Madame Lavoisier kept detailed records and sketches of her husband's work. She also designed and etched the plates for his masterwork: *Traite Elementaire de Chimie (Treatise on Chemical Elements*), published in 1789.

In 1793, a dramatic change in Madame Lavoisier's life occurred as her husband was arrested by the ruling Jacobin government. Madame Lavoisier wrote letters and begged for his release to no avail. After he and her father were guillotined in 1794, Madame Lavoisier was also arrested and spent sixty-five days in prison. After her release, the government changed, and she was allowed to gather together all of her late husband's works and materials.

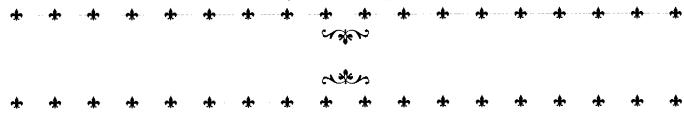
After her husband's death, Madame Lavoisier had several suitors, including one of the founders of the major chemical company DuPont de Nemours who had been closely connected with her former husband as a result of their mutual interest in munitions and chemical explosives.



Sketch of Lavoisier conducting an experiment on human respiration. This drawing is by Madame Lavoisier who shows herself taking notes at a nearby table.



In 1805, when she was forty-seven years old, she married another scientist, the international traveler and inventor Benjamin Thompson, Count Rumford, but the marriage lasted for only four years. She lived alone until her death at the age of seventy-eight.



Radioactivity and Nuclear Structure

Yow did experiments by Ernest Ruther-YOford, James Chadwick, Antoine Henri Becquerel, and Pierre and Marie Curie help to establish correct ideas about radioactivity and nuclear structure?

In 1896, Henri Becquerel became the first person to identify radioactive decay. In a famous experiment, Becquerel placed minerals containing uranium near unexposed photographic plates. When subsequently developed, the plates showed images of the mineral specimens that had been formed by the radiation that had passed through the light seals on the plates.

In 1898, Pierre and Marie Curie followed up on this discovery by isolating two elements from two tons of uranium ore (pitchblende) after a number of chemical separations. The few milligrams of the two highly radioactive chemical elements were named Polonium and Radium.¹²

In 1920, Lord Rutherford (formerly Ernest Rutherford) and his students carried out key experiments in which they bombarded thin gold foil with alpha particles from a

radioactive source. Most particles went straight through the foil; a few were strongly deflected by what could only be a tiny, highly charged, massive central nucleus in an atom. Butherford also proved that alpha particles were part of helium gas by sealing a radioactive substance emitting alpha particles in a glass tube and showing that helium gas was slowly produced. Rutherford's model of the atom thus consisted of a heavy central nucleus that was positively charged and was surrounded by enough negatively charged electrons to make the atom neutral.

James Chadwick repeated experiments carried out by Marie Curie's daughter, Irène Joliot-Curie (with her husband, Frederic Joliot-Curie), in 1932. In the experiment, the Joliot-Curies had used a strong source of alpha particles to bombard a beryllium foil, obtaining a "neutral radiation" that they interpreted as gamma radiation (photons). Chadwick showed that the product of the beryllium reaction was a neutral particle with a mass large enough to knock hydrogen atoms out of paraffin wax. The neutron had been discovered. From all these experiments, a model of the nuclear structure of the atom was formed.¹³

The Periodic Table and Associated Periodicity

mitri Mendeleev was a Russian scientist who decided that all of the identified chemical elements could be organized in a logical way. What characteristics did Mendeleev use to organize the chemical elements into a table? What did he do about elements that didn't seem to fit into the table?

Mendeleev decided to organize the known chemical elements by collecting information on their physical and chemical properties. In Mendeleev's first publication, issued in 1869, he placed similar elements in rows and columns in increasing order of their atomic weights. In this way, he discovered that certain properties repeated. He named this the Periodic System.

There were a few problems with Mendeleev's system, as some elements didn't seem to belong, in terms of properties, where this ordering system placed them. Mendeleev made the insightful judgment that the properties (physical melting

Ueber die Besiehungen der Rigenschaften zu den Atomgewichten der Elemente. Von D. Men delejeff. — Ordnet man Elemente nach zunehmenden Atomgewichten in verticale Reihen so, dass die Horizontalreihen analoge Elemente enthalten, wieder nach zunehmendem Atomgewicht geordnet, so erhält man folgende Zusammenstellung, aus der sich einige allgemeinere Folgerungen ableiten hassen. $Ti = 50 \qquad Z_T = 90 \qquad \stackrel{?}{\sim} -180 \\ V = 51 \qquad Nb = 94 \qquad Ta = 192$

1. Die nach der Grösse des Atomgewichts geordaeten Elemente zeigen eine stufenweise Abanderung in den Eigenschaften.

2. Chemisch-analoge Elemente haben entweder übereinstimmende Atomgewichte (Pt. Ir. 0a), oder letztere nehmen gleichviel zu (K. Rb. Ca).

3. Das Anordsen nach den Atomgewichten entspricht der Werthigkeit der Elemente und bis zu einem gewissen Grade der Verschiedenheit im chemischen Verhalen, z. B. Id. Be, B. C. N. O. F.

4. Die in der Natur verbreitetsten Elemente haben kleine Atomgewichte

The world's first view of Mendeleev's Periodic Table an extract from the main German chemistry periodical of the time, Zeitschrift für Chemic, 1869.

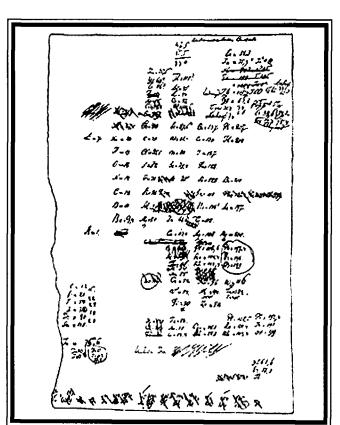
IMAGE CREDIT: HISTORY OF THE PERIODIC TABLE:

< HTTP://WWW.RSC.ORG/FDUCATION/TEACHERS/LEARNNET/
PERIODICTABLE/PRE16/DEVELOP/MENDELEEV.HTM>.

PHOTOGRAPH BY GORDON WOODS, REPRODUCED BY
PERMISSION OF THE ROYAL SOCIETY OF CHEMISTRY.

or boiling points and chemical reactivity) of these elements were likely correct, but their atomic weights might be incorrect. Indeed, when their atomic weights were re-measured, some elements fit better into the periodic scheme. In other instances, Mendeleev needed to "skip" a position to better line up properties. Again, his insight led him to propose the existence of "missing" elements. In this way, he proposed "eka-aluminum," which was later discovered as gallium and which fit in the same column in the next row below aluminum.¹⁴

Much more recently, it was found that three "problem" pairs of elements—Ar-K, Co-Ni, and Te-I—that appeared to be in the wrong order of atomic weights are in that order because the particular ratios of isotopes that make up these natural elements happen to give an average atomic mass that is in reverse order. In 1914, Henry Moseley, working in Rutherford's laboratory, proved that the correct order was obtained by using atomic numbers rather than atomic masses. •



The first draft of the Periodic System of the Elements by Mendeleev.





Section II:

The Structure of Matter— Independent Research Copics

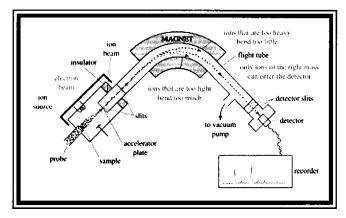
Mass Spectrometry

One way that chemists identify atoms and compounds is by measuring their mass. In modern laboratories this is done by using an instrument called a mass spectrometer. In your independent research, you should discover how mass spectrometers measure the masses of atoms and compounds.

A mass spectrometer is able to separate and measure atoms and compounds because moving charged species (ions) of different mass (and energy) are affected differently by magnetic or electric fields. A mass spectrometer has three basic components:

- An ion source where compounds or atoms are made into (usually positive) ions;
- 2. A mass analyzer where the ions are accelerated in magnetic fields and take different pathways;
- A detector that measures the number of ions of each mass that are present.

In one type of mass spectrometer, the ions are sent into a curved path by using a curved magnet. Another type of



Basic schematic of a magnetic sector mass spectrometer with electron impact source.



mass spectrometer that is commonly used at airports for security purposes features a straight pathway used with a cycling magnetic field. Notice that the substances must first be made into a gas and then introduced into a vacuum. The scanning of different masses is accomplished by varying the magnetic field and/or the detector position.



Properties and Importance of Commonly Recognized Isotopes—²H, ¹⁴C, ⁶⁰Co

sotopes are important in chemistry, life sciences, and earth sciences. In your independent research, you should discover where ²H, an isotope of hydrogen, ¹⁴C, an isotope of carbon, and ⁶⁰₂₇Co, an isotope of cobalt, are found as well as how they are made. How are

they used? And, what properties of these isotopes have made them useful?

Remember that an isotope is a form of an element whose nucleus contains a different number of neutrons from an atom of that element, but has the same number of protons. Thus, an isotope has the same chemical properties as other atoms of that element because the number of protons (and electrons) determines the chemical properties of the atom.

Many isotopes exist in nature. For example, all forms of compounds containing hydrogen, such as water, contain small amounts of deuterium, the isotope of hydrogen that contains a neutron in its nucleus and so is written as symbol ²H to distinguish it from regular hydrogen, symbol ¹H. The actual amount is 1 atom of deuterium for every 6500 atoms of hydrogen. Since deuterium can be separated and measured using a mass spectrometer, deuterium can be used as a "tracer" to find out how chemical reactions of hydrogen occur by enhancing the amount of deuterium (above the normal 1/6500 ratio) in a reactant and then following to see where deuterium shows up in the product(s). Deuterium may become very important as a fuel for fusion power production since it combines in a fusion reaction with another isotope of hydrogen, tritium, to release large amounts of energy.

¹⁴C is an isotope of carbon that is found together with most forms of carbon. It is formed in the upper atmosphere as a result of cosmic rays hitting nitrogen atoms. It mixes with atmospheric carbon dioxide and then becomes part of the biosphere, entering the bodies of all living systems. However, this isotope is not permanently stable and is therefore radioactive, with a half-life of about 5,730 years.¹⁵

The most well-known use for ${}^{14}_{6}\mathrm{C}$ is the dating of materials containing carbon, such as wood or bones. When a living system dies, it ceases to maintain equilibrium with the ${}^{14}_{6}\mathrm{C}$ being produced by cosmic rays, and so the amount of the isotope decreases at the half-life rate. This means there will be one-half of the original amount in 5,730 years. Thus, by measuring the amount of ${}^{14}_{6}\mathrm{C}$ left, archeologists can determine when the material ceased to be alive.

Even though it is present in very small amounts, ¹⁴C can also be used as a tracer to determine what happens to carbon atoms in chemical and biochemical reactions because of its radioactivity. ¹⁴C was used to work out the detailed chemistry of photosynthesis and respiration reactions in plants and animals. It is also being used to study possible global climate change effects, as climatologists look at how rapidly earbon from carbon dioxide cycles through various reservoirs in the biogeochemical cycle of carbon.

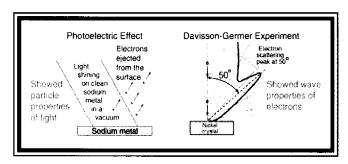
The isotope of cobalt $^{60}_{27}$ Co does not occur in nature, but can be made in nuclear reactors from cobalt metal. It is highly radioactive and has a half-life of 5.3 years. The radiation emitted as it decays is very penetrating to the human body and also will kill living cells. It has thus been used to kill cancerous tumor cells. The radiation will also kill harmful bacteria, so the isotope is used to sterilize foods for longer storage and medical equipment prior to use in surgery. The penetrating power of the radiation from $^{60}_{27}$ Co is greater in steel than that from X-rays, and so its radiation is used to examine steel components and welds for possible flaws. Since it darkens photographic film in the same way as X-rays, photographs of the welds or other objects can be made. ¹⁶



Wave and Particle Nature of the Electron and Photon

All matter is now known to exhibit both particle and wave properties. In your independent research, you should discover a good definition/explanation of the "wave-particle duality" of matter. You should also be able to identify and explain at least one experiment that shows that waves of light also have particle properties, and one experiment that shows that electrons also have wave properties.

The mysterious properties of light first alerted scientists to the notion that wavelike properties and particle properties could be exhibited simultaneously in experiments. Today we believe all matter can be represented by wave equations,



The photoelectric effect demonstrates the particle nature of light while the wave properties of electrons were shown in the classic Davisson-Germer experiment.



but recognize that matter also exhibits properties typical of a particle. The field of quantum physics deals with such issues. Particles are sometimes thought of as "wave packets" that can essentially arrive instantaneously to give the effect of a particle arriving. Light behaving as a particle was demonstrated most clearly in the photoelectric effect, where a light "photon" transfers its energy to an electron, which then is emitted from a metal surface. Nowadays, this phenomenon is very common in photocells in digital cameras. The wave properties of electrons were shown in the classic Davisson-Germer experiment where electrons scattered at preferred angles from a nickel crystal.



Electronegativity

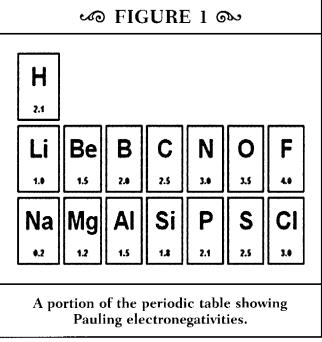
In your independent research, you should learn the definition of electronegativity and gain a general understanding of the concept of electronegativity. What are electronegativity's trends across periods and down columns of the periodic table? How is electronegativity useful for predicting the kind of chemical bonding that an atom will form?

Electronegativity is a measure of one atom's attraction of electrons from the adjacent atom to which it is chemically bonded. Linus Pauling (1901–94) devised a method of arriving at a single numerical value for relative electronegativity, and this value is referred to as a Pauling electronegativity. A few such values are exhibited in the small portion of the periodic table shown in Figure 1.

The higher the value of the Pauling electronegativity is, the greater the attraction for neighboring electrons. Notice that the trend in values is to increase from left to right and to decrease from top to bottom. This is a measure of how much the positive charge on the nucleus penetrates to the outside of the atom, enabling the attraction of nearby negative electrons.

You can think of electronegativity, or EN, as a way to measure the winner in a "tug of war" for bonding electrons. If the EN values of the two atoms forming a bond are widely different, then the one with the higher value will win the electrons away from the other, forming an ionic bond. So,

Na–F, with a difference of 4.0-0.2=3.8, would be predicted to be an ionic compound, or Na⁺ – F⁻. On the other hand N–O, with a difference of 3.5-3.0 or 0.5, would be expected to be an electron sharing or covalent compound, but with a small *dipole moment*. If EN values are identical, as in H₂ or F₂, then a truly equal situation gives rise to a non-polar, covalent compound.



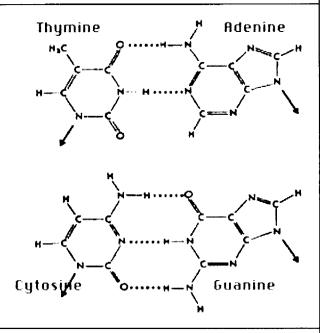


The Importance of Hydrogen Bonding in Living Systems

In your independent research, you should learn to identify and explain the key role

that hydrogen bonding plays in determining the DNA structure in living cells.

ൃ FIGURE 2 യ



Two sample base-pairings from a DNA molecule.

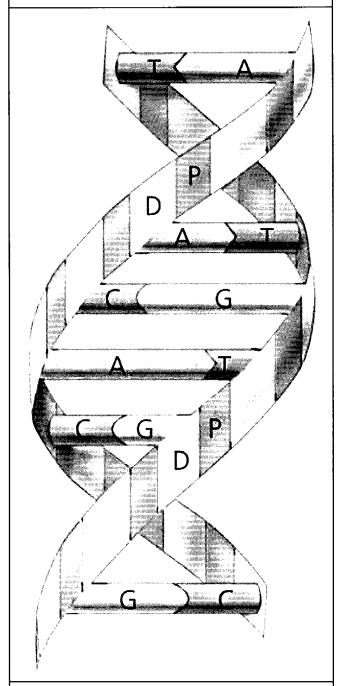
IMAGE CREDIT: JOHN W. KIMBALL. COPYRIGHT ©2008 JOHN W. KIMBALL. ALL RIGHTS RESERVED.

Hydrogen bonds are especially strong dipole-dipole interactions between hydrogen atoms and strongly electronegative atoms, such as oxygen or nitrogen. The DNA molecule consists of chains of nucleic acids. Each of these contains the necessary ingredients for hydrogen bonding, namely: H atoms, O atoms, and N atoms. Two such "pairings" are shown in Figure 2.

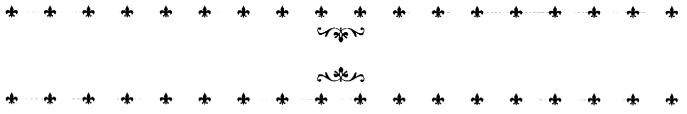
In the 1950s, James Watson and Francis Crick established a model of DNA based on X-ray studies of DNA by Rosalind Franklin and Maurice Wilkins, which suggested that the hydrogen bonds between specific parts of the molecules caused DNA to form a double helix structure as is shown in Figure 3.

Subsequent studies confirmed this and established mechanisms by which the genetic code contained in the ordering of the monomer nucleic components of the original long strand could be passed on.

ശ FIGURE 3 യ



The structure of part of a DNA double helix.



The Formation of Molecular Orbitals

In your independent research, you should learn the answers to the following

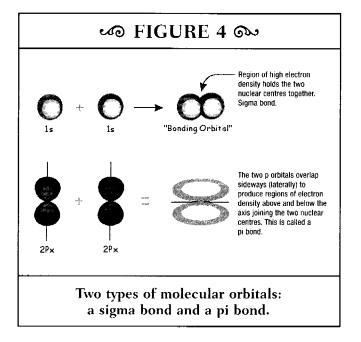
questions:

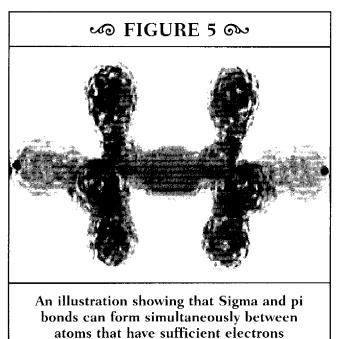
1. What are electron molecular orbitals?

2. What is the difference between sigma and pi molecular orbitals?

3. How are orbitals thought to be arranged in N₂, O₂, F₂, and CO₂?

When two or more atoms combine to form a chemical molecule, the bonding electrons take up new physical arrangements between the atoms, pulling the atoms together and forming the bond. Theoretical (mathematical) models can trace out the "electron waves" that constitute these electron positions and shapes, which are called "molecular orbitals," or MOs for short. The simplest model suggests that the original atomic orbitals combine or overlap to form



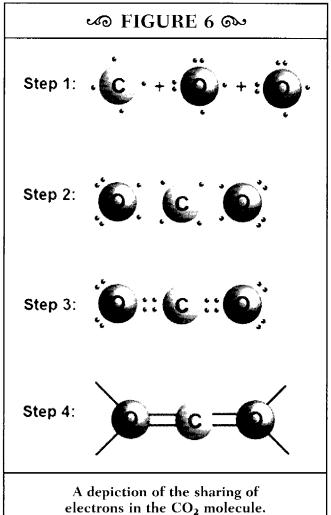


in the appropriate atomic orbitals.

the new MOs. Two kinds of overlap are predicted: overlap in which the new MO is concentrated along an imaginary line connecting the atoms, called a *sigma MO* or *sigma bond*, and overlap where the electron wave shape is concentrated between the atoms, but away from the center line. This second type of overlap is called a *pi MO* or *pi bond*. The diagrams pictured in Figure 4 show how these orbitals and bonds are envisioned, with the atomic orbitals on the left and the MO's that are formed on the right.

Note that the types of MO that form depend on the atomic orbital (AO) in which the electrons exist prior to bonding. In the examples shown, 1s AO's can overlap to form a sigma MO, whereas p AO's can overlap to form a pi MO since they have the correct orientation. The $2p_{\chi}$ AO's (aligned in the x-coordinate direction) can form a pi bond as shown.

Sigma and pi bonds often form simultaneously between atoms that have sufficient electrons in the appropriate atomic orbitals. Thus F_2 , with 14 valence electrons, needs to share only one pair of electrons to satisfy a valence octet on each atom and thus forms one sigma bond. O_2 , with only 12 valence electrons, needs to share two pairs to complete its atomic octets and thus forms one sigma and one pi bond. N_2 , with only 10 valence electrons, shares three pairs of



electrons in one sigma and two pi bonds as is illustrated in Figure 5.

With CO₂, there are a total of $4 + (2 \times 6) = 16$ valence electrons, so to satisfy the octets on C and on each of the two O atoms, there will be one sigma and one pi bond (two pairs of shared electrons) between the carbon and each oxygen atom. The way the electrons are shared (without the orbital shapes) is shown in Figure 6.

In the final step, each line represents a pair of electrons.

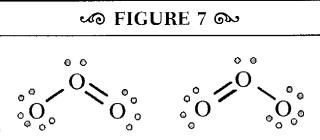
The full theory concerning molecular orbitals is much more complex and detailed than is presented here and includes the idea that orbitals can be both non-bonding or anti-bonding as well as "bonding."



The Resonance Concept Model

on your independent research, you should I discover what the resonance concept model is when applied to molecular structures and should be able to explain how resonance is used to rationalize the equal nature of bonds in the compounds O_3 and SO_3 .

Resonance applies in some instances to bonding in molecules with more than two atoms. It was introduced to explain the experimental finding that bond properties



These Lewis structures are equivalent except for the placement of the electrons (i.e., the location of the double bond).

DIAGRAM COURTESY OF DR. MICHAEL BLABER.

∞ FIGURE 8 ∞

This figure indicates that the ozone molecule is described by an average of the two Lewis structures (i.e., the resonance forms).

DIAGRAM COURTESY OF DR. MICHAEL BLABER.

ൃ FIGURE 9 യ

Bonding in an O₃ molecule, with partial charges shown.

∞ FIGURE 10 ∞

Bonding in the molecule SO₃.

(length and strength of bonds) were equal, even when insufficient valence electrons were available to form bonds and satisfy each atom's octet requirement. This is most readily explained with an example such as O₃. ¹⁸ This molecule has eighteen valence electrons. However, experiments show only one type of "bond" exists between the oxygens. So, is the bonding double to the right or the left? (See Figure 7.)

This question is resolved in the resonance model by assuming that both exist, as is shown in Figure 8.

The original idea was that somehow the molecule oscillated between the two, hence the terminology of "resonance." However, now we know that the bonding is truly equivalent and could be thought of best as 1.5 bonds on

each side. ¹⁹ This concept is represented in Figure 9, which has partial charges added.

The molecule SO₃ can be treated similarly since all three bonds in this molecule are experimentally identical. The final result can be represented as is shown in Figure 10. The dashed bonds represent ½ of a bond, so each resulting bond total for the link between the two atoms is 1½ bonds.

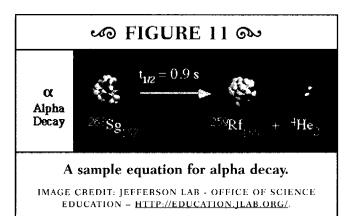
With detailed molecular orbital treatments that allow for sigma and pi bond formation and include "delocalized" orbitals that can bond more than two atoms together with a pair of electrons, a very modern theory has come to replace the resonance model.



Decay Equations and Predicting Products of Decays

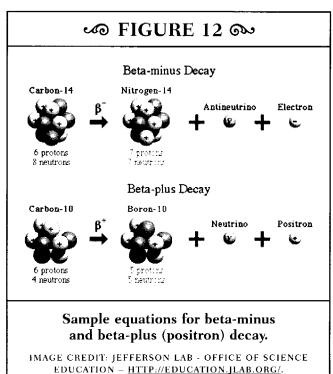
Adioactive decay occurs by well known and predictable pathways. Your independent research should enable you to write typical decay equations for alpha, beta-minus, and positron decay of an unstable atom. It should also enable you to predict the products of these decays if you are given the identity of the parent nuclide and the decay type.

Unstable nuclei result in radioactive decay. Examples of decay equations have been given in the *USAD Science Besource Guide*. One more example of each is provided here. Alpha decay results in the loss of two neutrons and two protons from the parent nucleus. Nuclei generally break up by alpha decay if they are very large, so the very stable alpha particle can form within the nucleus and tunnel its way out. Nuclei larger than bismuth (Z = 83) frequently break down by alpha decay. FIGURE 11 shows a sample equation for alpha decay.



Beta minus decay results in the loss of one neutron and the gain of one proton from the parent nucleus. The antineutrino shares energy with the emitted electron. Positron (or beta plus) decay results in the gain of one neutron and the loss of one proton from the parent nucleus. The neutrino shares energy with the positron. FIGURE 12 shows sample equations for beta-minus and beta-plus (positron) decay.

Predictions of beta decay are based on the understanding that a nucleus is unstable because of an imbalance between the number of neutrons and the number of pro-



tons. Generally, if there are too many neutrons, beta-minus decay (as was shown for ¹⁴C, which has six protons and eight neutrons) with electron emission occurs. In this way, the nucleus converts a neutron to a proton, which results in a closer to 1:1 ratio of protons to neutrons, such as in

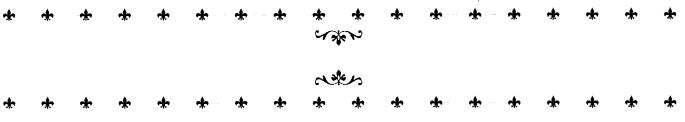
¹⁴N, which has a 7:7 ratio of protons to neutrons. If too few neutrons are present, positron (positively charged electron) emission occurs. This was shown for ¹⁰C, which has six protons and only four neutrons. The product is ¹⁰B, which has a more stable 5:5 ratio of neutrons to protons.



Alpha Bombardment Reactions

A suclear transformations can also be initiated by bombarding one type of atom with another atom or with a fundamental particle, such as an alpha particle or a neutron. The first nuclear transformation performed was carried out using alpha particle bombardment. Your research should enable you to write a balanced nuclear reaction for an alpha bombardment reaction.

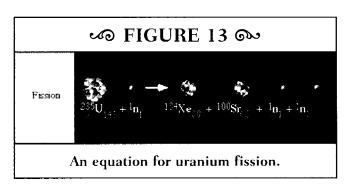
In 1919, Ernest Rutherford announced that he had shown that the bombardment of nitrogen atoms with alpha particles created oxygen atoms. The balanced equation for that reaction looks like this: ${}_{2}^{4}He + {}_{7}^{14}N \rightarrow {}_{8}^{17}O + {}_{1}^{1}H$. Note that the sum of the upper numbers (mass numbers) on one side of the equation is equal to the sum of the upper numbers (mass numbers) on the other side of the equation. The same is true for the lower atomic numbers. This is done to conserve neutrons and protons, which do not convert in alpha decay. (Be aware, however, that they do convert one to another in beta decay.)



Fission and Fusion Reactions

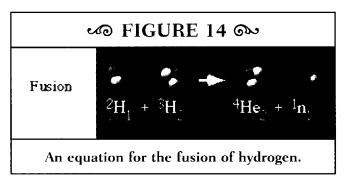
Franium fission and the fusion reaction of deuterium (²H) with tritium (³H) are both possible sources of energy for human use. Your independent research should aim to answer the following questions:

1. What happens in fission of the uranium isotope ²³⁵U?



2. What happens when fusion of deuterium with tritium occurs?

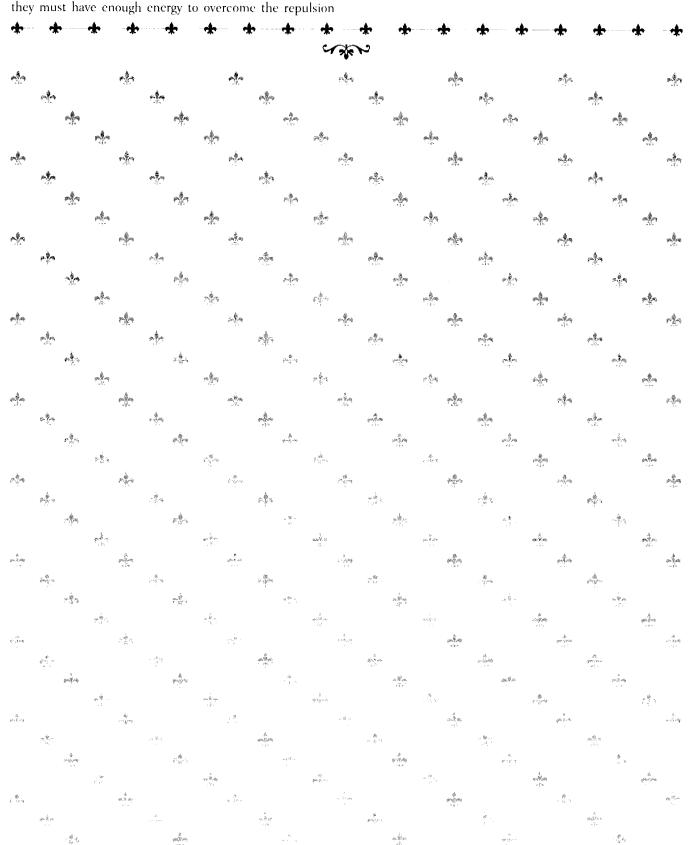
During uranium fission in a nuclear reactor, the uranium is hit by a free neutron, whose binding energy provides the energy for the breakup of the uranium. Each reaction can yield different products, but generally one product has a mass of about 130 amu, and the other has a mass of about 100 amu. In addition, two or three neutrons are



released. All of these products fly apart with a large amount of kinetic energy. This is heat that can be used to raise the temperature of water, make steam, and drive the turbine of an electric power generator. One possible balanced equation for uranium fission is shown in Figure 13.

In order for the two nuclei of hydrogen isotopes to fuse, they must have enough energy to overcome the repulsion

force of the two positive charges. This is a great deal of energy, which is why it has not yet been possible for this process to be carried out on a large enough scale to produce electric power. The balanced equation for the fusion reaction is shown in FIGURE 14.





Section III:

States of Matter— Independent Research Copics

Partial Pressures and Correction of Gas Volumes Collected over Water

The effect of changing pressure, volume, and temperature for mixtures of ideally behaving gases is more difficult than for making such changes to a single gas. However, Dalton's Law of partial pressures enables us to consider each gas separately. In your independent research, you should find out how Dalton's Law is used to explain how mixtures of gases follow the gas laws that we have examined. To isolate a gas, scientists often must use water to trap the gas in a container. Your research should also answer the question of how the true pressure of the gas is determined if water is present.

In gases the gas particles move rapidly and far apart. The pressure these particles exert is due to their collisions with the walls of the container. Assuming that the particles behave ideally and do not stick together or react with one another, adding other gas particles simply increases the collision rate in proportion to the number of gas molecules added. So, each gas exerts its "own" pressure on the walls, and the total pressure is proportional to the number of particles of each gas (usually expressed as the number of moles of gas present in the container). We can then express the amount of each gas as its "mole fraction"—the moles of gas A, for example, divided by the sum of the moles of all the gasses present. This could be written in equation form as follows:

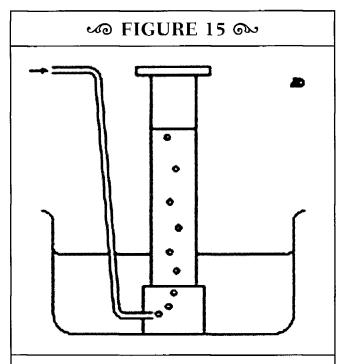
mole fraction (A) =
$$\frac{n_A}{n_A + n_B + n_C + \dots}$$
.

As a consequence of the ideal gas law, PV = nRT, pressure, P, is directly proportional to the number of moles of gas, n. So, we can also write:

mole fraction A =
$$\frac{P_A}{P_A + P_B + P_C + \dots}$$

This expression is Dalton's Law.

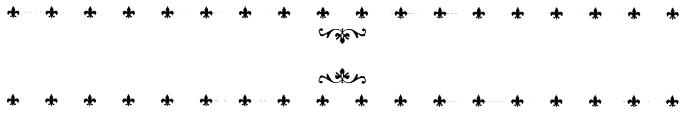
In a closed system, such as a jar of gas over water, the water contributes some pressure as a result of its *vapor* pressure. There is equilibrium between liquid water and



In a closed system, such as a jar of gas over water, the water contributes some pressure as a result of its vapor pressure. its vapor above the water, and the value of the water vapor pressure only depends on the temperature of the liquid. Therefore, the water vapor pressure can be looked up in a standard table.

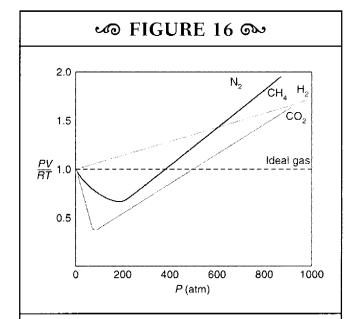
For example, if a gas such as nitrogen is being collected in the apparatus shown in Figure 15, and the gas pressure is measured to be 760.0 mm Hg, and the temperature is

20°C, we can simply refer to a table that tells us the water vapor pressure at 20°C is 17.5 mm Hg. Thus, the actual pressure of the nitrogen is only 760.0 - 17.5 or 742.5 mm Hg. This is useful because if the volume, V, is known, then the number of moles of nitrogen can be calculated using PV = nRT (remembering to use T in Kelvin, not Celsius, and the appropriate units for R).



The Behavior of Gases under Extreme Conditions

and pressure, most gases exhibit behavior that doesn't agree with the ideal gas equation. In your independent research, you should explore what happens if gas molecules do not have characteristics exactly similar to the assumptions made in the Kinetic Molecular Theory. How do some common gases such as He, O₂, CH₄, and CO₂ behave under conditions of extreme high and low temperatures and pressures? What is the explanation for the differences in the way they behave? Why



Plotting the experimentally determined value of (PV/RT) for exactly one mole of various real gases as a function of pressure, P, shows a deviation from the value that would be expected from an ideal gas.

is this important, for example, in our choice of substances to use as refrigerants?

The three key assumptions made in Kinetic Molecular theory (KMT) are as follows:

- 1. Gas molecules have no volume;
- 2. There are no intermolecular forces between the molecules;
- 3. Collisions are truly elastic—only kinetic energy is transferred.

If gas pressures are low and the volume is large and molecules are moving very rapidly (i.e., the temperature is high), then the KMT conditions are satisfied for most common gases. However, in the opposite conditions of high pressure, low volume, and low temperature, most gases do not behave ideally as is shown in the plot in Figure 16, which compares the ideal value of 1.0 for PV/RT for 1 mole of the gas as the pressure is increased.

Generally this behavior is measured by how well the gas pressure agrees with the rearranged formula P = nRT/V. Johannes van der Waals (1837–1923) developed a useful equation to monitor the behavior of non-ideal gases, which is now known by his name and corrects for the two main effects as is shown below:

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$
correction for volume of molecules
(decreases volume as a function of the number of molecules)
(decreases pressure as volume decreases and the number of molecules increases)

Van der Waals introduced two parameters, a, and b, that can be measured and used in his equation to calculate the "true" pressure. The values for a and b for many gases can be found in tables in textbooks and on the internet; the smaller the values, the more ideal the gas behavior is. The value for a is a correction value for the attraction that gas molecules may have for each other during collisions while b is a correction value for the volume of the gas. Table 1 shows just a few such values.

✓ TABLE 1 🍛		
SUBSTANCE	a (L ² atm/mol ²)	b (L/mol)
He	0.0341	0.0237
02	1.36	0.0318
CH ₄	2.25	0.0428
CO ₂	3.59	0.0427
NH ₃	4.23	0.0371

A refrigerator works by compressing a gas to make it into a liquid. The liquid is then allowed to evaporate through

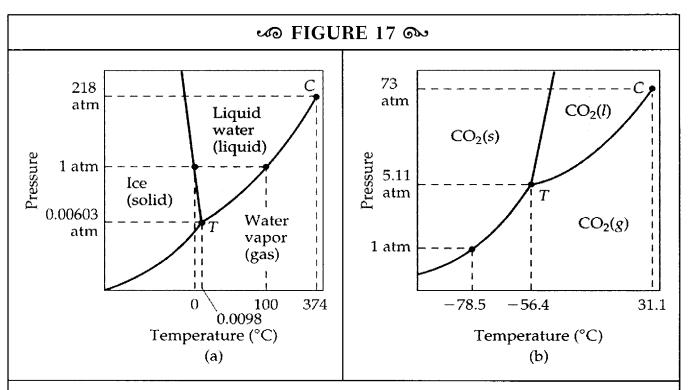
a small hole and, in doing so, cools itself and its immediate surroundings. Conservation of energy is maintained since compressing the gas causes heating that balances the cooling. In a refrigerator, this heat is dissipated into the surrounding room. Obviously, if the gas does not easily liquefy, then it is a poor choice for a refrigerator liquid. Therefore, gases with large van der Waals constants are good choices for refrigerator liquids. For many years, chlorofluorocarbons (CFC's) were chosen as having excellent properties for refrigeration; however, these caused environmental damage by destroying Earth's ozone layer and so are no longer used. Ammonia (NH₃) and carbon dioxide (CO₂) are good substitutes.



Carbon Dioxide

Carbon dioxide has a more normal phase diagram than water. Your research into carbon dioxide and its phase diagram should be directed to answer the following questions:

- 1. Why is it so difficult to observe liquid carbon dioxide?
- 2. Why is super-critical carbon dioxide becoming an important commercial substance?



A comparison of the phase diagrams of water and carbon dioxide.

IMAGE CREDIT: CHEMISTRY, THE CENTRAL SCIENCE, 11TH EDITION, BY THEODORE BROWN, EUGENE LEMAY, AND BRUCE BURSTEN, PRENTICE HALL, 2009. COPYRIGHT © PEARSON PRENTICE HALL, INC.

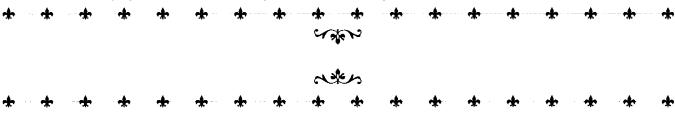
The diagrams in FIGURE 17 show a comparison of the phase diagrams of water and carbon dioxide.

Note that there is a difference in the scales used and that the scales are not linear. For CO_2 , the triple point is at 5.11 atmospheres and $-56.4^{\circ}C$. This means that liquid CO_2 cannot be observed unless the pressure is at least 5.11 times the normal atmospheric pressure on Earth and unless the temperature is well below normal temperatures seen on Earth.

Chemists and industrialists have been seeking substances that can be good solvents for applications such as making new medications and removing grease stains from clothes. Carbon dioxide in its liquid state is a good solvent for many such applications. However, carbon dioxide must be maintained at high pressures to remain a liquid. Above

the critical point, found at point C on the diagrams in Figure 17, for CO₂ at 73 atm and 31.1°C, CO₂ becomes supercritical. This means that its behavior has qualities of both a gas and a liquid. It retains the density of a liquid but becomes as mobile as a gas, both of which are ideal properties for a solvent.

In recent years, engineers have designed apparatus that can maintain the necessary pressure and temperature for the use of supercritical CO_2 in many industries. The main advantage is that the solvent is easily removed by reducing the pressure to slightly below the critical value, so the CO_2 just boils away. In most designs, the CO_2 is captured and recycled, so it doesn't add to the CO_2 burden in the atmosphere.



Raoult's Law and Colligative Properties

Colligative properties of solutions are properties that depend on the amounts of substances present, i.e., the concentrations of solutions. These properties include boiling point (temperature), freezing point, and osmotic pressure. The French chemist François Raoult (1830–1901) formulated specific rules to explain this behavior that became known as Raoult's Law.

In your independent research, you should investigate Raoult's Law and find out how it is used to explain colligative property changes when a nonvolatile solute, such as sugar or an ionic salt, is dissolved in a solution. Specifically, you should be able to explain how the solute changes the temperatures at which the solution boils or freezes. You should also be able to explain how and why a salt such as calcium chloride (CaCl₂) has a greater effect, per mole of dissolved solute, than a salt such as NaCl. You should also learn how to explain why table salt (NaCl) can be used in cold climates to reduce ice on roads, and you should also find out about some newer and better alternatives to this approach to ice reduction.

Additional research on solutions should lead you to understand and be able to explain how and why distillation works as a method for purifying water. What are some advantages and disadvantages of this method for use in providing drinking water, as with the desalinization of seawater?

François Raoult established that the key factor determining the physical properties of a solution was the relative number of moles of solute in the solution. For example, if you dissolve 1.80 grams (0.010 mol) of glucose sugar ($C_6H_{12}O_6$, molar mass = 180 g/mol) in 1 kilogram of water, you will change the freezing point of the water from 0.0000°C to -0.0186°C, and if you add ten times that amount (018.0 grams or 0.10 mol), you will change the freezing point by ten times as much, or to -0.186°C. If you use any other kind of sugar, you will get the same effect from 0.01 mol or 0.10 mol; the chemical doesn't matter, only the moles do. The same impact is seen on the boiling point, except that the temperature at which the solution boils is raised, rather than lowered, by a fixed (but different) amount.

The explanation for this lies in the effect that any solute has on the vapor pressure of a solvent as is shown in the phase diagram in FIGURE 18.

The solute particles interfere with the ability of solvent molecules to enter the vapor phase, thus shifting the necessary temperatures at which the phase changes will be observed. The diagram shows the shifts in the freezing point, ΔT_f , and boiling point, ΔT_b , of a solution compared to the pure solvent.

However, an intriguing effect is observed when salts are dissolved in water. In such cases, larger than expected changes occur, given the number of moles added. For example, 0.1 mole of sodium chloride, NaCl, added to

∞ FIGURE 18 ∞ 1 atm Liquid Pure liquid Pressure Solid Triple point Solution of solvent Pure solic solvent Boiling point Gas of solution Freezing point of solution Triple point Boiling point Freezing point of solution of solvent of solveni Temperature

This phase diagram depicts the effect of a solute on the vapor pressure of the solvent, showing the shifts in the freezing point, ΔT_f , and boiling point, ΔT_b , of a solution compared to the pure solvent.

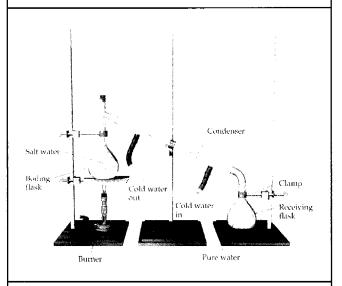
IMAGE CREDIT: CHEMISTRY, THE CENTRAL SCIENCE, 11TH EDITION, BY THEODORE BROWN, EUGENE LEMAY, AND BRUCE BURSTEN, PRENTICE HALL, 2009. COPYRIGHT ⊕ PEARSON PRENTICE HALL, INC.

water causes a change in boiling point twice that which would otherwise be expected. This is readily explained since NaCl completely ionizes in water, forming Na⁺ and Cl ions. Thus, there are two moles of ions present for every one mole of salt added. Therefore, the colligative property effects depend on the number of particle species present, not the moles of original salt. Calcium chloride, CaCl₂, produces three moles of ions per mole of calcium chloride in solution. Indeed, this is found to have three times the effect on freezing and boiling points than would be expected from just one mole.

The idea of adding salts to water or ice on roads to lower the freezing temperature and prevent or reduce ice formation has been around for a long time. Mostly sodium chloride has been used since it is available inexpensively. However, the subsequent salt solution run-off has been found to be harmful to roadside plants and animals and increases concrete damage. Calcium magnesium acetate (CaMg(CH₃COO)₂) has been proposed as a much less damaging alternative along with some other alternatives, but these are more expensive.

It is important to note that in all the solutions discussed above, the solute doesn't contribute anything to the vapor pressure above the solution. The vapor above the solution is pure solvent! So, if it can somehow be captured and removed, samples of pure solvent would be obtained, and the solution would gradually become more concentrated in solute. This is exactly the principle behind distillation as a means to purify solvents such as water. Impure or contami-

∽ FIGURE 19 ∞



A typical laboratory still for obtaining pure water.

IMAGE CREDIT: CHEMISTRY, THE CENTRAL SCIENCE, 11TH EDITION, BY THEODORE BROWN, EUGENE LEMAY, AND BRUCE BURSTEN, PRENTICE HALL, 2009. COPYRIGHT © PEARSON PRENTICE HALL, INC.

nated water cannot be used for a number of applications. Increasing supplies of pure water is becoming a major issue for an expanding human population and the agriculture on which humans depend for food. A typical laboratory still for obtaining pure water is shown in FIGURE 19. A commercial unit involves a large scaling up of such a device.

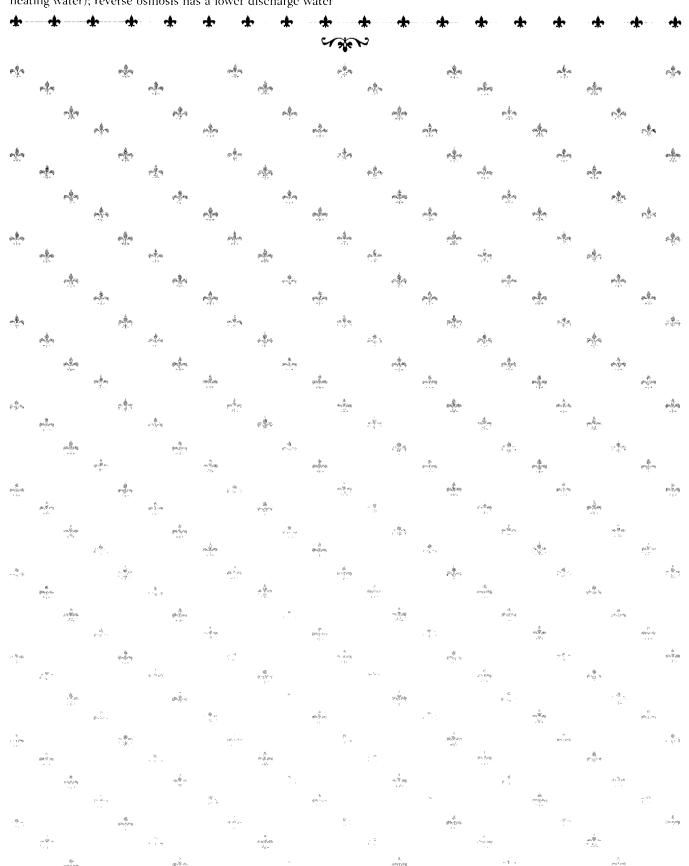
The most viable alternative to distillation is to use a process called *reverse osmosis*, which relies on a different colligative property of solutions. In reverse osmosis, water is pumped at high pressure through a semi-permeable membrane that allows water molecules to pass through but restricts impurity molecules, including salts, from passage. Pure water is then collected on the inside of the membrane tubes. The California Coastal Commission has published a comparison of different methods for the desalination of sea water for human and agricultural use. Proposed desalination operation in Carlsbad, California.

Methods of water purification/desalination must be compared for a given amount of pure water produced on the basis of several general as well as local factors, including:

- ✓ Energy used
- ✓ Pretreatment needed
- ₩aste to be discharged
- ✓ Product purity
- Maintenance frequency and costs

Advantages of distillation over reverse osmosis include the fact that with distillation it is easier to scale up to large sizes; there is less of a need for shut-downs or membrane cleaning; there is less pretreatment needed; and there is less waste to dispose of. Advantages of reverse osmosis over distillation include the fact that reverse osmosis has lower energy needs (pumping water uses less energy than heating water); reverse osmosis has a lower discharge water

temperature (which is less damaging to the ecosystem); reverse osmosis also has purer water output (no volatile contaminants) and does not require as large a plant as does distillation. \bigstar





Section IV:

Reactions— Independent Research Copics

Acid-Base Reactions and Salts

Some salts test acidic or basic when dissolved in water (i.e., they have a pH that is not equal to 7). This is a result of the ions in the salt undergoing a secondary reaction with the water. This secondary reaction is called hydrolysis. Your research should explore which salts make acidic solutions and why, and which salts make basic solutions and why. Is there a specific pattern that can enable a chemist to predict whether a particular salt will yield an acidic or basic solution when dissolved in water?

A salt is an ionic compound that is a product of the reaction between an acid and a base. When the salt dissolves in water, its ions can interact with water molecules in a reaction called *hydrolysis*. If hydrolysis results in the anion in the salt reacting with water to produce the conjugate acid of the anion and the hydroxide ion, then the solution will be basic. If, instead, the cation reacts significantly with water to form the conjugate base and H⁺, then the solution will be acidic. If neither ion reacts significantly, or if both react equally, then the solution will be neutral. An example of each scenario is given below.

(a) Basic Salt: Dissolving solid sodium acetate in water. Sodium and acetate ions are formed. The acetate ion (an

anion) accepts a proton from water, forming excess hydroxide ion:

$$CH_3COO^*(aq) + H_2O(l) \leftarrow CH_3COOH(aq) + OH^*(aq)$$

The conjugate acid produced, acetic acid, is a weak acid that does not ionize to a great extent. Since the acetate ion has accepted a proton, it has behaved as a base. The solution will have a pH > 7 as a result of the hydroxide ions produced. The sodium ions are "spectators." In general, anions of weak acids will form basic salts.

(b) Acidic Salt: Dissolving solid ammonium chloride in water. Ammonium and chloride ions are formed. The ammonium ion donates a proton to water, forming the hydronium ion:

$$NH_4^+(aq) + H_5O(l) + NH_3(aq) + H_3O^+(aq)$$

The conjugate base produced, ammonia, is a weak base that does not ionize to any great extent. Since the ammonium ion has donated a proton to water, it has behaved as an acid. The solution will have a pH < 7 as a result of the hydronium ions produced. The chloride ions are spectators. In general, cations of weak bases will form acidic salts.

(c) Neutral Salt: Dissolving sodium chloride in water. Sodium and chloride ions are produced. Neither reacts appreciably with water in an acid-base hydrolysis reaction, so the pH = 7, and hence it is a neutral solution:

$$Na^{+}(aq) + C\Gamma(aq) + H_2O(1) \rightarrow \text{no reaction}$$

These types of salts are formed from the cation of a strong base and the anion of a strong acid.

TABLE 2 യെ			
РΗ	CATION EXAMPLES	ANION EXAMPLES	
= 7, neutral	Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , Mg ²⁺ , Ca ²⁺	Cl ⁻ , Br ⁻ , I ⁻ , ClO ₄ ⁻ , BrO ₄ ⁻ , NO ₃ ⁻	
< 7, acidic	NH ₄ ⁺ , CH ₃ NH ₃ ⁺ , Cu ²⁺		
> 7, basic		F ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , CH ₃ COO ⁻	

TABLE 2 shows some typical cations and anions and the salts they will form.

Thus, to predict whether a salt will dissolve to form an acidic, basic, or neutral solution, one has to know if the ions composing the salt will undergo hydrolysis.



Precipitates

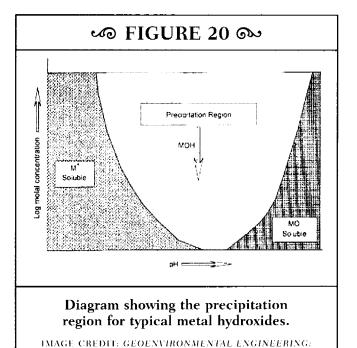
Come precipitates are dangerous for the environment. In your independent research, you should aim to identify at least two precipitates that are hazardous, and you should learn how they could be removed from the environment. Some precipitates are useful. In your research, you should aim to identify and explain at least one way in which a precipitate is useful to people.

The phenomenon of precipitation has been described as an equilibrium process in the *USAD Science Resource Guide*. A key feature that is important for the environment is that for many chemical substances, the range of conditions under which substances dissolve in water or precipitates is limited, as is shown in the diagram for typical metal hydroxides shown in FIGURE 20.

For example, the control of soil pH is important for plant growth. Unless nutrients dissolve, they are unavailable to plants, and so farmers must add acidic or basic substances to their soils to optimize the dissolution of nutrients. In some regions of the country, acid rain is responsible for lowering soil pH. This must be balanced by the addition of basic chemicals to neutralize the effects of the acid rain. Efforts to adjust soil pH may inhibit efforts to remove toxic contaminants that have been added to the environment by increasing their solubility.

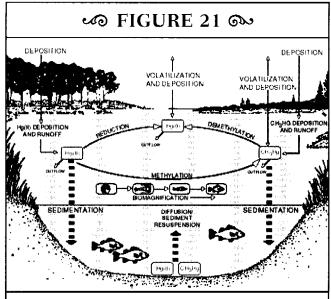
Perhaps the most well-known contaminant is mercury, which enters the environment as metallic mercury emitted into the atmosphere from fossil fuel power plants and enters into lakes and soils as waste from the use of mercury in electrolytic cells for the production of chemicals, such as chlorine. Improved practices have been able to reduce the release of mercury from electrolytic cells to quite low levels.

Mercury from the atmosphere enters the aquatic environment, precipitating in various forms which then cycle back into the water and the biosphere in complex ways, as is shown in Figure 21.



CONTAMINATED SOILS, POLLUTANT FATE, AND

MITIGATION, BY BAYMOND N. YONG, CRC PRESS, © 2001



The aquatic mercury cycle.

IMAGE CREDIT: CHEMISTRY, THE CENTRAL SCIENCE, 11TH EDITION, BY THEODORE BROWN, EUGENE LEMAY,

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Many other precipitates cause problems in the environment, including those being transported in mine run-off and toxic materials absorbed on iron hydroxide precipitate. One other source of harmful precipitates is in the atmosphere. Atmospheric particles, called particulates, enter the lungs where they may stick or exchange harmful components that damage lung tissue. Unfortunately, seemingly harmless particles, such as sea salt, can absorb other chemicals on their surfaces and transport them into the lungs.

Toxic substances are easier to bury or handle than solutions. So, using precipitation to remove dissolved toxic substances from large amounts of contaminated water is a common process. Care must then be taken to see that the precipitates are themselves carefully disposed of and cannot reenter the environment as particulates or by re-dissolving.

One example of this approach is the recovery of silver metal from used photographic chemicals. Before digital cameras became so widely used, an enormous number of photographs were processed. Almost all of these involved the use of silver halide salts. After the exposure and development of the image, which consisted of silver metal on paper or plastic, excess silver had to be removed in a process called fixing. Large amounts of silver were then in the waste solutions and were complexed with the chemical sodium thiosulfate. The silver could be precipitated as metallic silver by adding iron (in the form of steel wool) or as silver chloride by adding chloride ion. Subsequently, the silver could be melted into ingots, or the chloride could be dissolved in nitric acid, and the silver could be electrolytically plated.



Electroplating

Plectroplating is used in many industries. In your independent research, you should identify two different industries that use electroplating and explain how they do it. You should understand how much energy is needed and be able to show a calculation indicating how the energy added can be used to determine the number of grams of material that is electroplated.

Electroplating is the process of passing an electrical current through a solution containing a cation like Cu²⁺ and reducing it to Cu while coating an object with a thin layer of the metal. Often this coating adds corrosion protection and aesthetic qualities to a surface. For instance, in the auto and aerospace industries, plating with chromium provides hardness, corrosion and wear resistance, and enhances the appearance of a car. Tests show that chromium plated parts can last ten times longer than parts that are not plated.

The aerospace industry also uses gold plating on certain components used in rocket and space shuttle designs. This gold coating protects the parts from reacting with any other chemical substances on Earth or on other planets. It also helps since gold is highly reflective of solar radiation, the components to stay cooler. Almost 41 kilograms of gold were used in the construction of the space shuttle *Columbia*. Platinum, palladium, nickel, copper, silver, and rhodium

are metals that are often used in plating. The metal chosen depends on the qualities desired. Over many years, uses and fashions have changed. Many parts that used to be plated are now made from stainless steel. In the past, silver was often used on iron cutlery, but required frequent polishing or cleaning. Platinum gives a silver grey finish that resists corrosion and so is often used on sterling silver as well as on surgical instruments. Palladium finishes are often mistakenly called "white gold" and are used in expensive watches. Rhodium can be used to plate silver items to prevent tarnishing. Rhodium has a white color with high reflection, and it also resists body oils that can dull non-gold jewelry.

The amount of energy used in electroplating is dependent on the amount of material to be electroplated and the number of electrons that will be needed to reduce a metal ion to its element. Michael Faraday (1791-1867), an English chemist, determined that it took one mole of electrons to convert one mole of silver ion, Ag+, to silver metal. The electric charge on one mole of electrons was named the Faraday in his honor. To convert one mole of Cu²⁺ to copper metal, would take 2 Faradays of electrical change. Since chromium ion is Cr³⁺, it takes 3 Faradays to plate one mole, or 52 grams of chromium. The Faraday has 96,500 coulombs of charge, so 3 Faradays would have 96,500 × 3 = 289,500 coulombs of charge. If a voltage of about 2 volts is used for the plating, then the energy needed to create 52 grams of chromium plate is coulombs \times volts = 579,000 joules, or 579 kilojoules.

The Nernst Equation

The discussion of cell potentials in the USAD Science Resource Guide assumed that all reactants and products were in their "standard states." Walther Nernst (1864–1941) developed a way to make predictions about oxidation-reduction reactions. An equation known as the Nernst equation resulted from his work. Your independent research should lead you to learn about the Nernst equation and explore examples of how it is used to predict electrochemical phenomena under any reaction conditions.

The Nernst equation connects cell potentials to free energy changes for chemical reactions. It can be written to allow for any set of concentrations of reactants and products at any temperature. In its most fundamental form, it is written as follows:

$$E = E^0 - RT \ln Q/nF$$

However, most often we see it in a logarithm to the base 10 version, where the Faraday constant value, F, is included, the temperature is assumed to be 298 K (25°C), and the value of R has been included in appropriate units. So, the most useful version of the equation is written as follows:

$$E = E^0 - (0.0592 \log \Omega)/n$$

E is the cell potential in volts, E^0 is its value under standard state conditions (at 298K), n is the number of electrons transferred per unit reaction (moles per mole), and Q is the ratio of product concentrations to reactant concentrations.

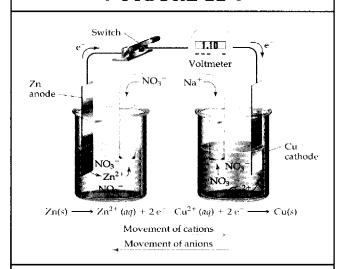
Let's consider an example in which this equation can be used. For the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, the E^0 of the cell shown in Figure 22 is + 1.10 volts, the moles of electrons transferred, n, per mole of Zinc is 2 and in the usual equilibrium constant formulation, and solids are not included in the concentrations ratios.

The Nernst expression is therefore:

$$E = +1.10 - 0.0592/2 \log [Zn^{2+}]/[Cu^{2+}].$$

So, if concentrations of solutions in the cell are known, the cell voltage can be calculated. For instance, if $[Zn^{2+}] = 0.50$ M, and $[Cu^{2+}] = 0.10$ M, then the cell voltage is predicted to be $+1.10 - 0.0296 \times \log 5 = +1.10 - .02 = +1.08$ volts. Notice that any time that the concentrations of reactants and products are equal, the cell voltage is the standard cell voltage. One other conclusion that can be drawn is that even if a cell has the same chemical in each compartment, if the concentrations are *not* equal, then there will be a cell voltage, even though E^0 is = 0. Such a cell is called a *concentration cell*.

ം FIGURE 22 യം



The Nernst equation connects cell potentials to free energy changes for chemical reactions.

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Hess's Law

A law called Hess's Law allows us to calculate enthalpy changes that have not

been measured based on our knowledge of other enthalpy changes that have been measured and using a cycle of reactions. In your independent research, you should find out about Hess's Law and learn how it is used.

Germain Hess (1802–50) formulated a principle known as Hess's Law, which states that the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps. This is essentially a restatement of the law of conservation of energy (that everything energy-wise must "add up"), and it is sometimes referred to as the law of constant heat summation. Hess's Law is especially useful for computing heat (enthalpy) changes for chemical processes that have not been measured directly. It can do this by using tabulations of data from related reactions.

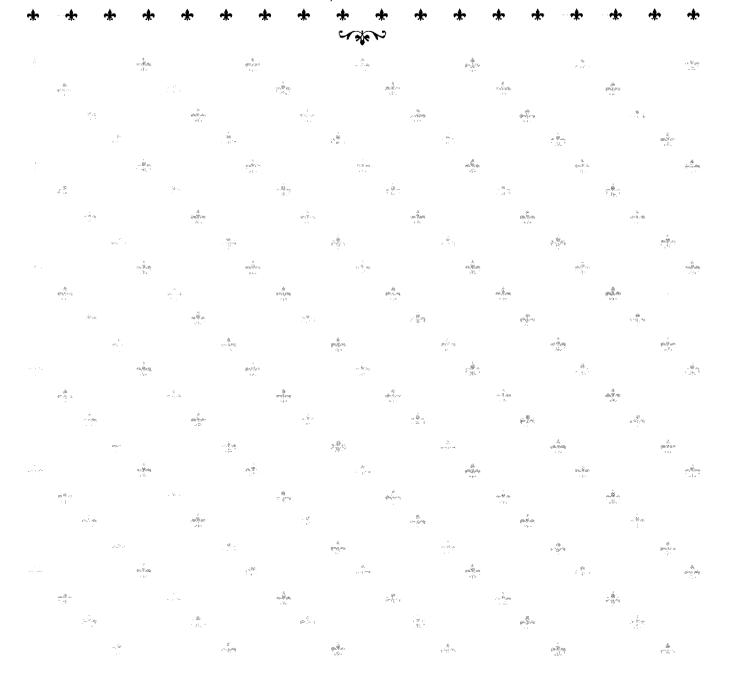
For example, it may be difficult to measure the enthalpy of formation of carbon monoxide, CO. The reaction equa-

tion for this process is as follows: $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$, and $\Delta H_f(CO)$ is desired.

However, enthalpy for the formation of CO_2 can easily be measured as can the enthalpy of oxidation of CO to CO_2 . The application of Hess's Law, with all values under standard conditions, enables us to make this calculation.

If $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H_f = -393$ kJ/mol, and CO + ½ $O_2 \rightarrow CO_2$, $\Delta H = -283$ kJ/mol, then subtracting the second equation from the first gives us: $C + \frac{1}{2} O_2 \rightarrow CO$ $\Delta H_f = -393 - (-283) = -110$ kJ/mol.

The equation shows the enthalpy of formation of CO to be –110 kJ/mol. Remember the negative sign indicates that this reaction is exothermic (i.e., heat is given to the surroundings). Many other examples of the use of Hess's Law are provided in standard chemistry textbooks and on Internet sites. *****





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