The problem sheets on the following pages are designed to show your understanding of some of the areas covered in the lecture courses. Each week, you should attempt all of the questions prior to the tutorial. The answers will be provided on the ‘Resources’ page, accessed via WebCT or the unit area on the First Year Chemistry website, at the end of the week before the tutorial. These should be used to check your answers, correct minor errors and to provide you with an idea of topics which you need to build on. Your tutor will ask you at the start of the tutorial for the topics and questions to go over.

In addition, your tutor will go over a number of past examination questions from the list given on the next page. Full solutions to these questions will not be provided online until the end of the semester.

Your performance in the tutorial quizzes and in the end of semester examination will be greatly enhanced by your attendance and involvement in the tutorial sessions.

In quiz weeks, you should attempt the sample quizzes, accessed via the ‘Tutorial Quizzes’ page on WebCT or on your unit area on the First Year Chemistry website. Your tutor will cover problems with these quiz questions prior to the actual quiz.
<table>
<thead>
<tr>
<th>Week 1 (taken from CHEM1001 papers)</th>
<th>Week 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 2005-J-5</td>
<td>• 2003-J-4 (iii)</td>
</tr>
<tr>
<td>• 2005-J-7 (1\textsuperscript{st} part only)</td>
<td>• 2004-J-3</td>
</tr>
<tr>
<td>• 2004-J-3 (1\textsuperscript{st} and 2\textsuperscript{nd} parts only)</td>
<td>• 2005-J-3</td>
</tr>
<tr>
<td>• 2003-J-2</td>
<td></td>
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<table>
<thead>
<tr>
<th>Week 3</th>
<th>Week 4</th>
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<tbody>
<tr>
<td>• 2003-J-3</td>
<td>• 2004-J-4 (iii)</td>
</tr>
<tr>
<td>• 2005-J-6 (ii)</td>
<td>• 2003-J-2 (iv)</td>
</tr>
<tr>
<td>• 2005-J-4 (ii)</td>
<td>• 2005-J-5 (i) (ii)</td>
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</tbody>
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<tr>
<th>Week 6</th>
<th>Week 7</th>
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<tbody>
<tr>
<td>• 2004-J-5</td>
<td>• 2005-J-5 (iii)</td>
</tr>
<tr>
<td>• 2005-J-7</td>
<td>• 2003-J-4 (i)</td>
</tr>
<tr>
<td>• 2004-J-2</td>
<td>• 2003-J-5 (ii)</td>
</tr>
<tr>
<td>• 2005-J-2</td>
<td>• 2004-J-4 (i)</td>
</tr>
<tr>
<td></td>
<td>• 2005-J-6 (i)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Week 8</th>
<th>Week 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 2003-J-2 (i)</td>
<td>• 2003-J-10 (ignore $\Delta G$ part)</td>
</tr>
<tr>
<td>• 2003-J-6 (i)</td>
<td>• 2004-J-11</td>
</tr>
<tr>
<td>• 2004-J-6</td>
<td>• 2005-J-8</td>
</tr>
<tr>
<td>• 2005-J-9</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Week 11</th>
<th>Week 13</th>
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<tbody>
<tr>
<td>• 2004-J-9</td>
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<tr>
<td>• 2005-J-10</td>
<td>• 2005-J-11</td>
</tr>
<tr>
<td>• 2004-J-7</td>
<td>• 2005-J-12</td>
</tr>
<tr>
<td></td>
<td>• 2003-J-5</td>
</tr>
</tbody>
</table>
There are a number of important learning resources available on your unit area on the First Year Chemistry website: http://firstyear.chem.usyd.edu.au/chem1901

Spend some time getting yourself familiar with this website and have a look at available resources, which include self help quizzes, games and calculators.

One of the most important resources is ChemCAL, an interactive tutorial/quiz program which covers most of the first year chemistry topics. Past students have found the program's interactive tutorials very useful. A link to ChemCAL is provided on the menu of all First Year Chemistry webpages. You log on to ChemCAL using your course code (‘1901’) as username, and helium as the password. (Note that none of the marks you receive in the various ChemCAL quizzes are ever recorded or assessed, and multiple attempts are OK!)

**Work through the ChemCAL module "Atomic and Nuclear Structure".**

Solutions to the problems below can be accessed from the ‘Resources’ page on your unit area on the First Year Chemistry website and on WebCT. If you have any problems, remember to ask your tutor for help during your first tutorial in week 1.

1. Classify each of the following as either *element*, *mixture* or *molecular compound*.

<table>
<thead>
<tr>
<th>liquid mercury</th>
<th>ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>neon gas</td>
<td>liquid nitrogen</td>
</tr>
<tr>
<td>milk</td>
<td>copper pipe</td>
</tr>
<tr>
<td>blood</td>
<td>air</td>
</tr>
<tr>
<td>gaseous CO₂</td>
<td>gaseous oxygen</td>
</tr>
<tr>
<td>solid sodium</td>
<td>brass</td>
</tr>
</tbody>
</table>

2. How many neutrons are there in one atom of $^{234}_{90}$Th?

3. Which of the following atoms and ions have exactly 10 electrons?
   - $O^{2-}$, He, Ar, $F^{-}$, Sr, $S^{2-}$, $Cl^{-}$, O, F, Ne

4. Which *one* of the following groups consists solely of *d*-block (transition) metals?
   - (a) carbon, silicon, germanium, lead, mercury
   - (b) arsenic, antimony, bismuth, tungsten, tellurium
   - (c) chromium, manganese, iron, cobalt, nickel
   - (d) aluminium, gallium, indium, thallium, bismuth
5. Which one of the following groups contains only elements that form anions?

(a) hydrogen, lithium, sodium, potassium
(b) boron, aluminium, gallium, indium
(c) helium, neon, argon, krypton
(d) fluorine, chlorine, bromine, iodine

6. What is the molecular mass of CH$_3$NH$_2$ and how many moles are there in 1 g?

7. What amount (in moles) of copper is involved when 24.9 g of crystalline CuSO$_4$·5H$_2$O is consumed in a reaction?

8. Calculate the atomic masses of (a) silicon and (b) tin from the isotope information provided below.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass of isotope (a.m.u.)</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{28}$Si</td>
<td>27.97693</td>
<td>92.21%</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>28.97649</td>
<td>4.70%</td>
</tr>
<tr>
<td>$^{30}$Si</td>
<td>29.97376</td>
<td>3.09%</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{112}$Sn</td>
<td>111.9048</td>
<td>0.97%</td>
</tr>
<tr>
<td>$^{114}$Sn</td>
<td>113.9028</td>
<td>0.65%</td>
</tr>
<tr>
<td>$^{115}$Sn</td>
<td>114.9033</td>
<td>0.36%</td>
</tr>
<tr>
<td>$^{116}$Sn</td>
<td>115.9017</td>
<td>14.53%</td>
</tr>
<tr>
<td>$^{117}$Sn</td>
<td>116.9030</td>
<td>7.68%</td>
</tr>
<tr>
<td>$^{118}$Sn</td>
<td>117.9016</td>
<td>24.22%</td>
</tr>
<tr>
<td>$^{119}$Sn</td>
<td>118.9033</td>
<td>8.58%</td>
</tr>
<tr>
<td>$^{120}$Sn</td>
<td>119.9022</td>
<td>32.59%</td>
</tr>
<tr>
<td>$^{122}$Sn</td>
<td>121.9034</td>
<td>4.63%</td>
</tr>
<tr>
<td>$^{124}$Sn</td>
<td>123.9053</td>
<td>5.79%</td>
</tr>
</tbody>
</table>

9. Naturally occurring chlorine consists of two main isotopes, $^{35}$Cl and $^{37}$Cl with masses 34.969 and 36.966 a.m.u respectively. Use the molar mass of chlorine of 35.453 g mol$^{-1}$ to calculate the relative abundance of these two isotopes.

10. Naturally occurring carbon consists of two main isotopes, $^{12}$C and $^{13}$C with masses 12.000 (exactly) and 13.003 a.m.u respectively. Use the molar mass of carbon of 12.011 g mol$^{-1}$ to calculate the relative abundance of these two isotopes.
1. Balance the following nuclear reactions and identify the missing nuclide or nuclear particle. (A periodic table is provided in the handbook.)

   \[ ^{14}_7 \text{N} + ^0_1 \text{n} \rightarrow ^{14}_6 \text{C} + ^1_1 \text{p} \]

   (a) \[ ^{20}_{10} \text{Ne} + ^0_1 \text{n} \rightarrow ^{20}_9 \text{F} + ? \]

   (b) \[ ^{15}_7 \text{N} + ^1_1 \text{p} \rightarrow ? + ^0_0 \text{n} \]

   (c) \[ ^{16}_8 \text{O} + ^1_1 \text{p} \rightarrow ^{17}_7 \text{N} + ? \]

2. \(^{19}_9 \text{F}\) is a stable nuclide. One of the following isotopes of fluorine undergoes radioactive decay by \(\beta^-\) emission and one decays by \(\beta^+\) emission. Predict which is which and write balanced equations for the decay reactions.

   (a) \(^{18}_9 \text{F}\)

   (b) \(^{20}_9 \text{F}\)

3. Calculate the radiocarbon age of a sample whose \(^{14}_6 \text{C}\) activity is 0.344 of a modern standard.

4. Calculate the molar activity of tritium (in Curie), given its half-life of 12.26 years.

   \[ [1 \text{ Ci} = 3.70 \times 10^{10} \text{ disintegrations per second.}] \]

5. Arrange the following elements in order of increasing ionisation energy:

   Ne, Na, C, Mg, N, F

6. Identify three elements whose atomic radii are similar to that of Li.

7. Identify the largest and smallest of all neutral atoms.

Optional.

(a) Read the following article on Einstein’s \(E = mc^2\) equation.

(b) Calculate (i) the change in mass, or mass defect, (in a.m.u.) which occurs when six \(^1\text{H}\) atoms and six neutrons fuse together to give one \(^{12}_6 \text{C}\) atom and (ii) the energy equivalent (in kJ mol\(^{-1}\)). [Masses in amu: \(^1\text{H} 1.007825, ^1\text{n} 1.008665, ^{12}_6 \text{C} 12.000000\)]
E = mc² for the Chemist: When Is Mass Conserved?

Richard S. Treptow
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In 1905 Albert Einstein derived an equation that expresses a relationship between mass and energy \((E = mc^2)\). These two quantities, which were previously thought to be independent of one another, became linked by \(E = mc^2\). In spite of its simplicity, the equation is often misinterpreted in textbooks and the popular science literature. Authors in both physics (2–12) and chemistry (13–19) have attempted over many years to correct the misconceptions. This article is one such effort. It asks to what extent is mass conserved in the reactions of physics and chemistry. The question can be used to challenge students and develop their language and critical thinking skills.

A Brief History and Apparent Contradictions

Although \(E = mc^2\) began as only a minor component of the theory of special relativity, it soon became its most widely recognized feature. As modern physics developed in the 20th century, nuclear and subatomic particle reactions were discovered that could be used to test the equation. The data they provided were often interpreted to mean that mass is simply one form of energy and that it can be converted into other forms, such as heat and work. If this were true, then mass could no longer be the conserved quantity it had always been.

Chemists viewed the famous equation from a distance and perhaps with some suspicion. The 18th century discoveries of Antoine Lavoisier provided convincing evidence that the reactants and products of a chemical reaction always have identical masses (20). Belief in conservation of matter enabled the atomic theory to be developed through the 19th century. Each chemical element was assigned an atomic mass that was assumed not to change as its atoms underwent chemical change. Any heat, work, or other energy produced by a reaction was said to have been derived from chemical energy. Mass did not enter into the discussion of energy. Chemists must have been tempted to conclude that \(E = mc^2\) had no relevance for their discipline.

Today’s general chemistry students have good reason to be confused about mass and energy conservation. Early in the course they are told that mass is neither created nor destroyed in chemical reactions. This principle is the basis for determining compound formulas and performing stoichiometric calculations. When thermochemistry is introduced, students learn that energy, too, cannot be created or destroyed, although it can be converted from one form to another. Thus, both properties of matter are said to have their own conservation law. Near the end of the course, nuclear reactions are introduced and everything appears to change. Mass is now said to be able to be converted into energy. If this is true, then both conservation laws must be abandoned or perhaps combined in some fashion. Is it possible that nuclear reactions and chemical reactions play by a different set of rules?

Mass–Energy and Its Conservation

The theory of special relativity boldly asserts that mass and energy are not the independent quantities they were once thought to be. Rather, they are two measures of a single quantity. Since that single quantity does not have its own name, it is called mass–energy, and the relationship between its two measures is known as mass–energy equivalence. We may regard \(c^2\) as a conversion factor that enables us to calculate one measurement from the other. Every mass has an energy-equivalent and every energy has a mass-equivalent. If a body emits energy to its surroundings it also emits a quantity of mass equivalent to that energy. The surroundings acquire both the energy and mass in the process.

Figure 1 illustrates several ways a reaction in a closed system can emit energy to its surroundings. Since the system is closed, we might ask how the surroundings are able to acquire mass along with the energy they receive. If the energy is received as heat, the increase in mass of the surroundings results because its atoms move faster as they warm. The mass of any body increases with its velocity according to special relativity. When the energy is received as electricity, the atoms in the surroundings move faster if the electrical energy produces heat or they acquire chemical energy if an electrolytic reaction occurs. In either case the atoms increase in mass. If the energy is received as electromagnetic radiation, the surroundings gain the mass of the emitted photons. A photon has an energy, \(E = h\nu\), where \(\nu\) is the frequency of the radiation. Hence, it has a mass, \(m = h\nu/c^2\). We should not be surprised to learn that a photon has mass. Astronomers re-
port that a beam of light is bent by gravity as it passes a mass-

sive body such as the sun. Recall also that light cannot es-
cape from the gravity of a black hole. Finally, if the energy is 
received as work, the surroundings gain mass because their 
potential energy increases. For example, a weight placed on 
the lid of the system will be lifted. The two-body system con-
sisting of the weight and the earth will acquire gravitational 
energy. In similar fashion, the mass of a rubber band increases 
a tiny degree as it is stretched. Energy in any form always 
has mass.

What became of the laws of conservation of mass and 
conservation of energy when physicists discovered that mass 
and energy are two measures of the same quantity? Each of 
the laws survived. It became clear, however, that they are only 
alternative expressions of a single law. The law of conserva-
tion of mass–energy requires that mass–energy cannot be cre-
ated or destroyed. It merges the two previously independent 
laws into one. A common misconception is that the conserva-
tion of mass–energy only requires that the total of mass 
and energy remains constant and that the two quantities can 
be converted into one another. In truth, taking the sum of 
mass and energy of a body is an exercise in double counting.

Incidentally, we chemists are well acquainted with other 
quantities that can be expressed by two different measures. 
The quantity of water in a beaker, for example, can be mea-
sured by its mass or its volume. The density of water is the 
conversion factor used to calculate one measurement from 
the other. Note that this conversion factor only enables us to 
change the units used to express the quantity of water. It does 
not imply that we can transform mass of water into volume 
of water. Similarly, we cannot transform mass into energy.

We will need a value for \( c^2 \) when performing calcula-
tions. The speed of light is 2.997925 \( \times 10^8 \) m/s in SI units. 
Therefore, \( c^2 = 8.98755 \times 10^{16} \) m\(^2\)/s\(^2\). If it is used as a con-
version factor, \( c^2 \) should be expressed in mass and energy 
units. Recall that the SI unit for energy is the joule, whose 
definition is 1 J = 1 kg m\(^2\)/s\(^2\). Thus, \( c^2 = 8.98755 \times 10^{16} \) 
J/kg. Table 1 lists other values for \( c^2 \) expressed in a variety 
of mass and energy units.

### Nuclear and Subatomic Particle Reactions

Mass–energy conservation can be experimentally tested 
by the energetic reactions of nuclei and subatomic particles. 
A frequently discussed reaction is the fission of a lithium-7 
nucleus when it is bombarded by a proton:

\[ ^1p + ^7Li \rightarrow ^{2}He + \text{kinetic energy} \]

The two alpha particles produced have kinetic energy that is 
quickly transferred to the surroundings. The reaction was first 
studied in the 1930s by Cockcroft and Walton (21). Table 2 
gives an accounting of mass–energy for the reaction. The ex-
perimental data on the first line are the rest masses of the 
nuclei and the net energy transferred to the surroundings (22). 
This net energy is equal to the kinetic energy of the alpha 
particles minus the kinetic energy of the bombarding proton. 
In the second line, each of these measurements has been con-
verted into its mass-equivalent or its energy-equivalent by use 
of the appropriate value of \( c^2 \) from Table 1.

Analysis of the data begins in the third line of the table. 
The total mass of the reactants and the total mass of the prod-
ucts have been calculated. The latter total includes the mass-
equivalent of the energy released to the surroundings. The 
two totals are identical within the certainty of the measure-
ments, hence, they demonstrate that mass is conserved in the 
reaction. Similarly, energy conservation is demonstrated in 
the fourth line, where the same totals have been calculated 
each measurement is now expressed as an energy. We should 
expect that mass and energy are both conserved, since they 
are two measures of the same quantity.

The last line of the table demonstrates how the experi-
mental data can be misinterpreted. The difference between 
the rest mass of the reactants and products has been calcu-

### Table 1. The Mass–Energy Conversion Factor Expressed in Various Units

<table>
<thead>
<tr>
<th>Mass Unit</th>
<th>Energy Unit</th>
<th>MeV</th>
<th>J</th>
<th>cal</th>
<th>kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>amu</td>
<td>931.494 MeV/amu</td>
<td>1.49242 ( \times 10^{-10} ) J/amu</td>
<td>3.56696 ( \times 10^{-11} ) cal/amu</td>
<td>4.14561 ( \times 10^{-17} ) kWh/amu</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>5.60959 ( \times 10^{26} ) MeV/g</td>
<td>8.98755 ( \times 10^{13} ) J/g</td>
<td>2.14808 ( \times 10^{13} ) cal/g</td>
<td>2.49654 ( \times 10^{-7} ) kWh/g</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Mass–Energy Account for the Nuclear Fission of Lithium-7

<table>
<thead>
<tr>
<th>Quantity</th>
<th>(^1p + ^7Li \rightarrow ^2He + ) energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Data</td>
<td>1.0073 amu</td>
</tr>
<tr>
<td>Mass-Equivalent or Energy-Equivalent</td>
<td>938.3 MeV</td>
</tr>
<tr>
<td>Demonstration of Mass Conservation</td>
<td>8.0217 amu</td>
</tr>
<tr>
<td>Demonstration of Energy Conservation</td>
<td>7472.2 MeV</td>
</tr>
<tr>
<td>Misconception of Mass Converted to Energy</td>
<td>0.0187 amu or 17.4 MeV</td>
</tr>
</tbody>
</table>
lated, and the energy equivalent of that lost mass is also entered. This calculated energy agrees well with the energy released to the surroundings. We should not conclude, however, that mass is converted or transformed into energy. Recall that the energy released to the surroundings carries mass with it. Mass is conserved in the reaction; it does not become energy.

It is useful to examine the equations that apply to the mass-energy accounting just discussed. Consider the general reaction

\[ A + B \rightarrow 2C + \text{energy} \]

Conservation of mass requires that the particle masses, \( M_1 \) and \( M_2 \), and the energy released to the surroundings, \( E \), follow the equation

\[ M_1 + M_2 = 2M + \frac{E}{c^2} \]

If we multiply by \( c^2 \) we obtain the requirement for conservation of energy:

\[ M_1 c^2 + M_2 c^2 = 2M c^2 + E \]

This equation can be rearranged to give

\[ (M_1 + M_2 - 2M)c^2 = E \]

Each of these equations is confirmed by the experimental data of Table 2. Note that the last of the equations affirms that the mass lost by the reacting system has an energy-equivalent equal to the energy gained by the surroundings. It does not imply, however, that mass has been converted into energy.

An analogy from everyday life can be used to explain why mass may appear to be converted into energy in reactions. Imagine the process illustrated in Figure 2 involving a bag full of gold coins. An experiment is performed in which the bag is weighed, two coins are removed from it, and it is weighed again. From the data shown in the figure it can be determined that each coin has a mass of 24 g. Hence, the conversion factor, 1 coin per 24 g, could be used to convert any measure of mass into the equivalent number of coins.

Both mass and the number of coins are conserved in the experiment. These two measures are simply alternative ways of expressing quantities of gold. It would be incorrect to conclude that mass has been converted into coins in the experiment, although a quick glance at the data in the figure might give that impression.

The most energetic of all reactions are those in which matter and antimatter undergo mutual annihilation. Consider the reaction between an electron and a positron to produce two photons:

\[ e^- + e^+ \rightarrow 2h\nu \]

Since the reacting particles are annihilated, all their mass is lost. Mass conservation is maintained nonetheless because the lost mass is carried by the photons, and it is finally acquired by the surroundings when the photons are absorbed. If we choose to define matter in such a way that it includes protons and electrons but not photons, then we can say that matter has been destroyed in this reaction. Mass, however, is not destroyed.

### Chemical Reactions

Chemical reactions are much less energetic than the reactions discussed above. Nevertheless, they are not exempt from the requirement of mass-energy conservation. When chemical reactants undergo a reaction that emits energy, they must lose an equivalent quantity of mass. Let us illustrate the process with a reaction well known for its release of energy, the explosion of nitroglycerine. The mass lost by the reactants can be calculated from chemical thermodynamics most easily if we imagine the reaction to begin and end with all substances in their standard states and at 25 °C:

\[ 4C_3H_7N_3O_9(l) \rightarrow 6N_2(g) + 12CO(g) + 10H_2O(l) + 7O_2(g) \]

Using standard enthalpies of formation (23) we obtain \( \Delta H \approx -2700 \text{ kJ} \). Since the reaction occurs at constant pressure, the relationship \( \Delta E = \Delta H - P\Delta V \) applies. This equation states that the energy lost by the reacting system is the sum of the heat it emits and the work it does. The explosive power of nitroglycerine is largely due to the work done on the surroundings by the rapid expansion of the hot gases formed. The approximation \( P\Delta V = \Delta nRT \), where \( \Delta n \) is the change in the chemical amount (number of moles) of gas, gives \( P\Delta V = 62 \text{ kJ} \). Therefore, \( \Delta E = -2762 \text{ kJ} \). Applying the appropriate mass-energy conversion factor we find that the energy lost is equivalent to \( 3.074 \times 10^8 \text{ g} \). In summary, the products of the reaction have 2762 kJ less energy and 3.074 \( \times 10^8 \) g less mass than the reactants.

The loss of mass that accompanies the reaction just discussed is too small to be detected by even the best measuring instruments, and the same is true for all chemical reactions. This explains why chemists in the laboratory have never found an exception to the principle handed down by Lavoisier that no change of mass occurs in the reacting matter. Strictly speaking, however, the mass of the matter in the reacting sys-
tem is not exactly constant. In recognition of this fact we should say that no detectable change of mass occurs in the reacting matter.

The gold coin analogy discussed earlier can be changed in such a way to explain why the mass of reacting matter in chemical reactions appears not to change. Figure 3 illustrates a process in which two gold coins are now removed from a truck containing a very large quantity of coins. The truck mass is so large that it appears to be unchanged in the process. The fact that each coin has a mass of 24 g is still true, but it cannot be deduced from the available data. The mass of gold in the truck is not exactly conserved, but the data available give that impression.

**Mass Defect of Nuclei and Molecules**

General chemistry textbooks commonly introduce $E = mc^2$ when discussing the stability of atomic nuclei. All nuclei have less mass than the protons and neutrons of which they are composed. The mass defect of a nucleus is the mass lost when it is formed from these nucleons. The simplest example would be the formation of hydrogen-2:

$$^1p + ^1n \rightarrow ^2H + \text{energy}$$

The rest masses of a proton and neutron are 1.007276 amu and 1.008665 amu, respectively, and that of an $^2H$ nucleus is 2.013553 amu (23). Hence, the mass defect is 0.002388 amu. This mass has an energy-equivalent of $3.564 \times 10^{-13}$ J. This is the energy released by the reaction. It is called the binding energy of the nucleus because it would be required to break the bond between the two nucleons.

We can extend the concept of mass defect and binding energy to chemistry. Consider the bonding of atoms required to form a methane molecule:

$$\text{C} + 4\text{H} \rightarrow \text{CH}_4 + \text{energy}$$

The energy released by this reaction is $2.916 \times 10^{-18}$ J/molecule (24). This chemical binding energy has a mass-equivalent of $1.954 \times 10^{-8}$ amu. Thus, a methane molecule has a chemical mass defect of $1.954 \times 10^{-8}$ amu. Its mass is that much less than of the atoms of which it is composed. Figure 4 illustrates the mass defect of the $^2H$ nucleus and the CH$_4$ molecule. The $^2H$ nucleus has 0.12% less mass than its nucleons, whereas the CH$_4$ molecule has only 0.00031% less mass than its atoms.

The carbon-12 atom is special in that its mass is set by definition. The rest mass of $^{12}\text{C}$ is exactly 12 amu. We can calculate the mass of the atom under other conditions, such as when it has gained kinetic energy by being warmed or when it has lost chemical energy owing to bonding to other carbon atoms to produce graphite or diamond. Such calculations have been previously reported (16) and the results are summarized in Table 3. Graphite and diamond can be said to have a mass defect. Although the defect is insignificant for practical purposes, we chemists should occasionally remind ourselves that the mass of an atom depends upon its chemical state.

![Figure 3](image-url)  
**Figure 3.** Experiment in which two gold coins are removed from a truck full of coins. The mass of gold in the truck appears to be constant because it decreases by a quantity too small to be detected.

![Figure 4](image-url)  
**Figure 4.** The mass defect of (A) an $^2H$ nucleus and (B) a CH$_4$ molecule demonstrated by a hypothetical experiment using a double-pan balance.

<table>
<thead>
<tr>
<th>Physical State</th>
<th>Atomic Mass/amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated atoms at rest</td>
<td>12.0000000000000</td>
</tr>
<tr>
<td>Isolated atoms at 298 K</td>
<td>12.0000000000045</td>
</tr>
<tr>
<td>Graphite at 298 K</td>
<td>11.99999999992116</td>
</tr>
<tr>
<td>Diamond at 298 K</td>
<td>11.9999999992137</td>
</tr>
</tbody>
</table>

Table 3. Atomic Mass of Carbon-12 in Various Chemical States
Fraction of Mass Lost

Any reaction that emits energy to its surroundings can be characterized by the fraction of mass lost by the reactants in the process. If we use the definition \( \Delta m = m_{\text{products}} - m_{\text{reactants}} \), then the mass lost is \( -\Delta m \), and the fraction of mass lost is \( -\Delta m/m_{\text{reactants}} \). Figure 5 displays the fraction of mass lost for various reactions on an exponential plot. The figure includes several reactions we have discussed. Also included are \(^2\!\!H\) fusion, \(^{235}\!\!U\) fission, hydrogen gas combustion, and the freezing of water.

The figure shows that reactions differ greatly in their fraction of mass lost and, hence, in the quantity of energy they emit. At the top of the figure is the highly energetic annihilation reaction followed by three nuclear reactions. At the bottom are three chemical reactions and a change of physical state. As we have discussed, the mass lost by these less-energetic reactions must be calculated from the energy lost; it cannot be measured directly.

Equations Speak for Themselves

Let us pause to ask what any mathematical equation means when it states that two quantities are equal. It does not imply that one quantity can be converted into another. For example, when a ball is thrown straight up into the air its kinetic energy, KE, is changed into potential energy, PE, as it rises. The equation that expresses that fact is

\[
\text{KE} + \text{PE} = \text{constant}
\]

It is clearly of a different form. Recall that the equation we are discussing is \( E = mc^2 \); it is not \( E + mc^2 = \text{constant} \). In summary, equations will speak for themselves if we are willing to listen.

Laws and Principles

We can now formulate a universal set of natural laws and also a principle useful in the practice of chemistry. The first and most comprehensive law is the


This law has no known exceptions. Since mass–energy can be measured by either mass or energy, it can be made more specific through two corollaries:

Corollary A. Law of Conservation of Mass: Mass cannot be created or destroyed.

Corollary B. Law of Conservation of Energy: Energy cannot be created or destroyed.

Both the reacting system and its surroundings must be considered when applying these three laws. They pertain to all the reactions of both physics and chemistry. A special situation arises when the requirement of conservation of mass is applied to chemical reactions:

Principle of Constant Mass: Chemical reactions occur with no detectable change in the mass of the reacting matter.

This principle applies to the reacting system only. It is the modern update of Lavoisier’s principle of conservation of matter. Its usefulness to the practice of chemistry is undeniable. It should not be classified as a law, however, because it only speaks about what is detectable. It does not express a universal truth.

Summary and Suggestions

The question asked in the title of this article has a simple answer: Mass is always conserved if we take into account both the reacting system and its surroundings. Mass is lost by the reacting system in any process that emits energy, but an equal quantity is acquired by the surroundings. Energy is conserved as surely as mass is. In fact, mass and energy are merely alter-
native measures of the single quantity known as mass–energy. The equation $E = mc^2$ enables us to calculate the energy-equivalent of any mass or the mass-equivalent of any energy.

Discussions of nuclear and subatomic particle reactions often lead to the misconception that mass has been converted into energy. In truth, a full accounting of both the reacting system and its surroundings will show that both mass and energy have been conserved. At best, the claim that mass can be converted into energy is a simplification that focuses attention on the most recognizable features of a reaction. If taken literally, however, it is incorrect.

In chemical reactions the mass lost by the reacting system is always too small to be detectable. This is true even for reactions that emit an easily measured quantity of energy to their surroundings. We should not conclude, however, that these reactions are exempt from mass–energy equivalence. Of course, the fact that the mass of the reacting matter is constant for all practical purposes greatly simplifies the practice of chemistry.

At what point should these concepts be introduced into the traditional general chemistry course? When atomic mass, the elemental composition of compounds and reaction stoichiometry are introduced, students need to understand that for all practical purposes the mass of an atom does not change with its chemical environment. At this time, the principle of constant mass should be introduced. Later in the course when the subject of thermodynamics enters, students need to know that energy is conserved when it is transformed from one form to another. The law of conservation of energy makes this clear. Finally, when nuclear binding energies and nuclear reaction energies are discussed late in the course, the subject of mass–energy equivalence should be presented along with the law of mass–energy conservation and its corollaries. The beauty of $E = mc^2$ can then be appreciated.

**Literature Cited**

1. Calculate the velocity and the wavelength of an electron with a kinetic energy of 100 eV. (Note that kinetic energy \( = \frac{p^2}{2m} \) with \( p = \) momentum and \( m = \) mass.)

2. Using the x-ray wavelength data provided below, construct a plot like that of Moseley, and hence determine the principle x-ray wavelength of chromium (a missing element).

<table>
<thead>
<tr>
<th>element</th>
<th>20Ca</th>
<th>22Ti</th>
<th>23V</th>
<th>25Mn</th>
<th>26Fe</th>
<th>28Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength (nm)</td>
<td>0.336</td>
<td>0.275</td>
<td>0.250</td>
<td>0.211</td>
<td>0.194</td>
<td>0.166</td>
</tr>
</tbody>
</table>

3. Calculate the largest energy gap between any two adjacent energy levels in He\(^+\) using the expression below for the energy level of an electron with quantum number \( n \) in a hydrogen-like atom.

\[
E_n = -\frac{E_R Z^2}{n^2} \quad \text{where} \quad E_R = 2.18 \times 10^{-18} \text{ J}
\]

4. Sketch the radial part of the 2-D waveform shown below on the axes provided, and identify the nodes. ‘0’ denotes the centre of the drumhead and ‘\( r \)’ the perimeter.

5. Complete the table below by filling in the quantum numbers that describe the following atomic orbitals. The 4\( d \) orbital has been completed as an example.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>( n )</th>
<th>( l )</th>
<th>( m_l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4( d )</td>
<td>4</td>
<td>2</td>
<td>-2, -1, 0, 1, 2</td>
</tr>
<tr>
<td>1( s )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3( p )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5( d )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. Sketch the lobe representations of a 2\(p\) and a 3\(p\) orbital.

7. Write out the electron configurations for the following elements in the two formats shown for aluminium.

\[\text{e.g. } \text{Al} \quad [\text{Ne}]3s^2 \, 3p^1 \quad [\text{Ne}] \uparrow \downarrow \uparrow\]

(a) O
(b) Ga
(c) Fr

Optional.
(a) Read the following article on relativistic effects in Chemistry.
(b) Why is mercury a liquid at room temperature?
Why Is Mercury Liquid?

Or, Why Do Relativistic Effects Not Get into Chemistry Textbooks?

Lars J. Norby
Royal Military College of Canada, Kingston, ON, Canada K7K 5L0

That mercury is liquid at ambient temperatures has been known since ancient times. The Greek name Hydrgyrum = “watery silver” (hence the symbol Hg) and the Latin Argentum Vivum = “quick silver” show this as do the English and French names of the element alluding to Mercury, the fast-footed messenger of the Latin gods. The Alchemists certainly knew mercury very well, especially its ability to dissolve gold, to amalgamate. As a matter of fact, amalgamation of noble metals with subsequent thermal decomposition was a method of extracting such metals in use in the Mediterranean area already about 500 B.C. Probably all of us have, sometime, dropped a thermometer and tried to chase those evasive small droplets all over the floor. At room temperature there is no doubt that mercury is liquid. But why? When I ask students, or colleagues for that matter, the answer goes “hm... it is because... hm... it has such a low melting point!” No way!

Purpose
I have consulted a fair number of currently used textbooks and “bibles” of inorganic chemistry including Greenwood and Earnshaw (1) and Cotton and Wilkinson (2). Nowhere have I found an explanation of the well-known fact that Hg is liquid with the exception of Mackay and Mackay (3), who very briefly discuss this in a short section “Relativistic effects”. Cotton and Wilkinson do mention relativistic effects a few times, but they do not give any consistent account of the great influence of relativity on chemical properties. However, there is an embarrassingly large literature including several excellent articles in this very Journal on this and related problems. See Pykkö (4, 5) and Suggested Readings. “Embarrassing” to us teachers of chemistry, that is. How come this knowledge has not yet got into the mainstream textbooks?

The purpose of this article is to present a fresh constellation of experimental facts, theoretical calculations, and a discussion of the chemical bonding in mercury that hopefully throws some new light on a number of classical issues in inorganic chemistry.

Mercury and Gold
It is most interesting to compare mercury with gold since the two elements are “next-door neighbors” in the periodic table but have dramatically different properties. The melting points, for example, Au 1064 °C and Hg -39 °C, differ more than for any other pair of neighboring metals in the periodic table (except for Li–Be where the difference also is about 1100 °C but for a different reason). The densities, Au 19.32 and Hg 13.55 g cm⁻³, also differ more than anywhere else. The enthalpies of fusion are quite different, Au 12.8 and Hg 2.30 kJ mol⁻¹. However, the entropies of fusion are very similar, Au 9.29 and Hg 9.81 J K⁻¹ mol⁻¹, which demonstrates that here is actually “nothing wrong” with the thermodynamic data of Hg. They consistently speak the same language: the bonding forces are much weaker in Hg than in Au. These data just restate what we already know but do not explain why mercury is liquid at ambient temperatures.

The electrical properties of gold and mercury are quite different. Au is an excellent conductor with a conductivity of 426 kS m⁻¹. Hg, on the other hand, is a much poorer conductor with a conductivity of only 10.4 kS m⁻¹. (All data given in this article are taken from Greenwood and Earnshaw (1) unless otherwise stated.)

From a structural point of view we note that Cu, Ag, and Au have cubic and Zn and Cd (slightly distorted) hexagonal close-packed crystal structures. However, Hg is rhombohedrally distorted and the Hg–Hg distance in the less-than-close-packed planes is about 16% “too large”. Again, the metal–metal bonds in Hg are obviously weaker than they “should” be.

Although Au and Hg necessarily have very similar electron structures,

\[ \text{79Au(g) : } \text{54} \text{Xe} \text{4f}^4 \text{5d}^{10} \text{6s}^1 \]

\[ \text{80Hg(g) : } \text{56} \text{Xe} \text{4f}^4 \text{5d}^{10} \text{6s}^2 \]

we might expect that the slight difference, somehow, lies behind their strikingly different properties. How?

Anomalies
There are a number of unexpected periodic properties, at least unexpected from a systematic point of view, when we look at the elements past the rare earths. A familiar example is the striking similarity between Hf and Zr. The lanthanoid contraction is the usual explanation for this, which is caused by the filling of the 4f orbital group (generally called a “subshell”). 4f electrons do not shield the nuclear charge nearly as well as d or p electrons or even d electrons. One also speaks of the lesser penetration of the 4f orbitals, which means that the 14 protons that are added as we go along the rare earths are not fully shielded off by the 14 4f electrons. This leads to gradually larger effective nuclear charges and a corresponding contraction of the electron cloud. This is certainly a true effect that is largely responsible for 71Lu being about 0.03 Å smaller than 39Yb, although there are 32 more electrons within the volume of the lutetium ion. The lanthanoid contraction is usually also held responsible for the metallic radii of Ag and Au both being 1.44 Å and those of Cd and Hg both being 1.51 Å.

Why is Au gold-colored? Why is it not silver-colored? Why does Au have the highest electron affinity, -223 kJ mol⁻¹, outside the really electronegative elements? Higher than sulfur and almost as high as iodine. Why is Ti stable in the oxidation state +1, Pb in +II, and Bi in +III, while their congeners are more stable as +III, +IV and +V, respectively?

The lanthanoid contraction alone does not explain all of these anomalies, even if it is a very useful concept. The “inert 6s² pair” introduced by Sidgwick in 1933 is another idea invoked: see, for example, an inorganic chemistry classic like Phillips and Williams (6). However, this latter concept does not really explain why mercury is liquid or why Pb(II) is more stable than Pb(IV). To find the real cause of all those anomalies we will have to look into an entirely different realm of science, namely relativity and its influence on chemical properties.
Relativity

Einstein taught us with his special relativity theory of 1905 that the mass of any moving object increases with its speed,

\[ m_{\text{rel}} = m_{\text{rest}} \sqrt{1 - (v/c)^2} \]

Bohr calculated the speed of a 1s electron in the hydrogen atom in its ground state as 1/137 of the speed of light when it is orbiting at the Bohr radius 0.53 Å. This speed is so low that the relativistic mass is only 1.00003 times the rest mass. Although small, Sommerfeld took relativistic effects into account when, in 1916, he refined Bohr's model introducing elliptic trajectories. However, when we turn to the heavy elements 79Au, 80Hg, and onward, the situation is quite different. The expected average radial velocity for a 1s electron in an atom heavier than hydrogen is

\[ \langle v_r \rangle \approx (2/137)c \]

which for Hg means (80/137)c \approx 0.58c, or 58% of the speed of light. \( m_{\text{rel}} \) then becomes 1.23 \( m_{\text{rest}} \). This in turn means that the Bohr radius shrinks by 23%, since the mass of the electron enters in the denominator. Thus the 1s orbitals in Au and Hg contract very much. Because all orbitals must be orthogonal to one another, an almost equally large mass–velocity contraction occurs for 2s, 3s, 4s, 5s, 6s, and 7s orbitals as well. Now, in order to appreciate what really is going on we need to look into Paul Dirac's relativistic quantum mechanics.

Dirac Quantum Mechanics

Schrodinger quantum mechanics with its probability contours, node patterns, and energy levels familiar to all undergraduate students of chemistry is not adequate when treating the heavy elements. Within the framework of spin–orbit coupling we learn that the angular and spin quantum numbers \( j \) and \( s \) are “no good” for the heavy elements but that their vector sum \( j + s \) is still, so that we get \( j-s \) coupling instead of \( L-S \) (Russell–Saunders) coupling.

The electron spin was “invented” by the Dutch physicists Uhlenbeck and Goudsmit in 1925 to explain the fine structure of the hydrogen spectrum. The Stern and Gerlach experiment of 1922, where a beam of vaporized silver atoms was split in two by an applied external inhomogeneous magnetic field, seemed to prove this idea. The idea of electron spin, that we usually meet as part of the Pauli exclusion principle, is a postulate added to the Schrodinger quantum mechanics with its probability contours, node patterns, and energy levels familiar to all undergraduate students of chemistry is not adequate when treating the heavy elements. Within the framework of spin–orbit coupling we learn that the angular and spin quantum numbers \( j \) and \( s \) are “no good” for the heavy elements but that their vector sum \( j + s \) is still, so that we get \( j-s \) coupling instead of \( L-S \) (Russell–Saunders) coupling.

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The Darwin term is usually explicitly invoked in the “Pauli relativistic” treatment of the Schrödinger equation, which is less cumbersome to use than a pure Dirac model.

Relativistic Effects

In summary, following Dirac we may speak of three relativistic effects

1. \( s_{1/2} \) and \( p_{1/2} \) orbitals contract quite a lot but \( p_{3/2} \) to a much lesser extent.

2. This in turn induces an extension outward of \( d \) and \( f \) orbitals relative to \( s \) and \( p \) orbitals.

3. “Spin–orbit coupling” is actually the relativistic splitting of \( p \), \( d \), and \( f \) orbital energies. This effect becomes large for the heavier elements.

The sum of these effects becomes very important for Au and Hg, making the energy difference between the \( 5d_{5/2} \) and \( 6s_{1/2} \) orbitals much smaller, see below. There is actually at least one more relativistic effect to consider called the Darwin term, which accounts for the oscillatory motion of the electron (“Zitterbewegung”) that becomes important near the atom nucleus. This term gives \( s \) electrons higher energy and expands \( s \) orbitals, which partially counteracts the velocity–mass contraction. It is implicitly included in “effect 2” above. The Darwin term is usually explicitly invoked in the “Pauli relativistic” treatment of the Schrödinger equation, which is less cumbersome to use than a pure Dirac model.

Relativistic Calculations

Relativistic energy band structures for gold, see Takeda (7), and other heavy metals and alloys have been calculated by a variety of methods, see Pyykö (4, 5) and Christensen (8). Illustrations of such band-structure calculations are not easy to employ for the purpose of this article. They actually need Brillouin zone theory and a whole host of concomitant concepts to be fully appreciated. Figure 1 has been chosen instead as a simpler illustration of the main points to be made. It portrays the relativistic calculations on the molecular species \( \text{AgH(g)} \) and \( \text{AuH(g)} \) by Pyykö (9) and Pyykö and Desclaux (10). The energy differences between the \( 4d \) and \( 5s \) orbitals of Ag and \( 5d \) and \( 6s \) of Au are obviously quite different, although their nonrelativistic counterparts are very similar. There are differences, of course, between a free gaseous gold atom, or a AuH(g) molecule, and the crystalline solid, but the main features of the relativistic effects are still the same. For extensive discussions of this point see Christensen (8) and Koelling and MacDonald (11). Excellent articles on relativistic effects on gold chemistry have been given by Schwerdtfeger et al. (12, 13). First-principle calculations by Takeuchi et al. (14) demonstrate that the higher cohesion energy of gold compared to silver is a relativistic effect.

X-ray photoelectron spectroscopy (ESCA) experiments on Au and other heavy metals and alloys thereof have shown that relativistic calculations are much closer to observations than are nonrelativistic ones. On the basis of both experiments and calculations one can conclude that the metal–metal bonds in Au(s) are brought about by the single 6s electrons with a 5d admixture but (almost) no 6p.

In the analysis of anomalous periodic properties a problem still remains, for relativistic effects do not vary smoothly with \( Z \). They rather seem to culminate for 79Au. The relativistic velocity–mass contraction of the radius of the 6s orbital of the free Au(g) atom has been calculated to about 16% (8). Furthermore, the relativistic effects are overlaid with the lanthanoid contraction, which in itself is relativistic to about 15%, as well as with an analogous 5d orbital contraction. For the 6s electron in solid gold the total stabilization of 2.8 ev (270 kJ mol\(^{-1}\)) arises 2/3 from relativistic effects and 1/3
from the lanthanoid contraction. See Bagus et al. (15) and Christiansen et al. (16). The net result of all these effects is generally difficult to predict.

**Silver and Gold**

We are now able to explain several of the differences between Ag and Au. The color of Au arises when blue light is absorbed and 5d electrons are excited to the 6s level, or strictly speaking to the Fermi level, which lies just at the top of the conduction band. Silver, however, having a larger band gap absorbs in UV and appears colorless. The first ionization energy of Au is slightly larger than that of Ag, while the second and third are larger for Ag. Therefore, we more often encounter Ag(I) than Au(I) but Au(III) more frequently than Ag(III). Furthermore, Au shows more pronounced covalent bonding in its complexes thanks to d–s hybrid orbitals that are energetically more favored than in Ag. Figure 1 is in qualitative agreement with all of this. See also Deselaux and Pyykkö (17).

**Electron Affinity**

The high electron affinity of Au may be qualified in the following way. The 6s orbital has such a low energy that “it feels good”, according to Pyykkö and Deselaux (10), for an extra electron to jump in and fill it. Cole and Perdew (18) have calculated that relativistic effects boost the electron affinity of gold by as much as 65%. Relativistic effects also explain why Au$_2$(g) is such a surprisingly stable molecule having a dissociation energy of 221 kJ mol$^{-1}$, which is more than I$_2$(g) (151 kJ mol$^{-1}$) and just a bit less than the single-bond energy of Cl$_2$(g) (243 kJ mol$^{-1}$).

**Intermetallic Compounds**

The intermetallic compound CsAu is not a metallically conducting alloy but a red transparent semiconductor crystallizing with the CsCl structure. This is another example of the yearning for one more electron in the 6s orbital of Au. We see a tendency toward an ionic compound Cs$^+$.Au$^-$. Experimental data are reproduced in Figure 2, from Wertheim (19). Calculations of the electronic structure of CsAu by Christiansen and Kollar (20) confirm that the semiconductivity in this case is an altogether relativistic effect. Gold is here not unlike iodine and has been called a “pseudo-halogen”.

**Why Is Mercury Liquid?**

Now, how about the central question of this article? Why is mercury liquid? We may find the answer taking a detour to the gas phase and to Hg(I). Hg does not form any strong covalent single bonds comparable to Au$_2$. However, Hg$_2^{2+}$, which is isoelectronic with Au$_2$, is a very stable species indeed well known from both aqueous solution and solid compounds. In fact, calculations by Ziegler et al. (21) show that relativistic effects shorten the bonds as much as 16% in both Au$_2$ and Hg$_2^{2+}$, making the bonding distances shorter than in the analogous silver and cadmium species. To draw an analogy, one could say that the difference between gold forming a strongly bonded stable dimer molecule in the gas phase, Au$_2$(g), and mercury, which is unique among metals by being almost entirely monomeric in the gas phase Hg(g), is of the same nature as the difference between H$_2$(g) and He(g), which is strictly monomeric. The common explana-
tion is that He$_2$(g) does not exist because the third and the fourth valence electron would populate the antibonding 1s* orbital thus completely destabilizing a diatomic molecule. In Hg the relativistically contracted 6s orbital is filled, and therefore the two 6s electrons do not contribute much to the metal–metal bonds. This is obviously the opposite of gold. One must conclude that the bonding is brought about largely by van der Waals forces, see Fyper et al. (22), and probably also through weak 6p orbital interaction. This is why the Hg–Hg bond is so weak.

Incidentally, this also explains why the electrical conductivity is so much lower for mercury than for gold: the two 6s electrons are rather localized and contribute only little to the conduction band. Mercury could in the vein of this analogy be called a pseudo noble gas.

**Amalgamation**

Why does liquid mercury dissolve gold and form amalgam? What is the chemical bonding like in an amalgam? Why does Hg amalgamate well with Cu, Ag, Au, and the alkali metals? The reaction with sodium is well known from the chlor–alkali process, where an amalgam with about 0.5% Na by mass) is formed at the liquid mercury cathode. Why does it react with the ammonium radical NH$_4^+$? Why poorly or not at all with most transition metals? Let us try this for an answer. As mentioned in the introduction, it is easy to retrieve gold from amalgam by simply heating it, so the bonding forces between Hg and Au are not very strong. Consider a hypothetical gaseous molecular species HgAu(g). In analogy with He$_2^+$, which has been spectroscopically characterized, it would have a three-electron bond, Hg–Au, with two electrons in a bonding 6s orbital and one electron in an antibonding 6s* orbital. This would be weaker than the strong single bond in Au$_2$(g) but stronger than the bonds between Hg atoms. Silver and gold provide one electron per atom to the amalgam bonds. The same holds for the alkali metals. Most transition metals react poorly with mercury because they contribute two s electrons per atom, and we are back to the case of mercury itself; only very weak bonds would be possible. The ammonium radical also provides one electron to the bond with Hg. It seems that if the alloying metal contributes one electron per atom, a good amalgam is formed but not if it contributes two.

It should be clearly stated that no unambiguous calculations have yet proven the ideas discussed above. Detailed relativistic band calculations on solid mercury and amalgam are needed to substantiate these bonding ideas. To carry out such calculations, it is generally necessary to assume that the crystal structure of the metal is either cubic close-packed or body-centered cubic. The rhombohedral distortion in crystalline mercury is quite far from cccp, which therefore would be a rather poor approximation. In the binary system Au–Hg no intermetallic phase richer in mercury than Au$_2$Hg has been confirmed. This stoichiometric compound has a hexagonal crystal structure and melts incongruently at 122 °C. The solid solubility of Au in Hg is negligible. See Rolfe and Hume–Rothery (23). Mercury-rich amalgams are therefore more or less well-crystallized two-phase mixtures of Au$_2$Hg and Hg. Relativistic calculations on liquid mercury, where the structure of the liquid (a cluster of eight nearest neighbors at 3.0 Å) is taken into account, would likewise be most useful.

**The Inert 6s$^2$ Pair**

Finally, as a last example of relativistic effects on heavy metal chemistry let us compare TI and In. Although the radius of the TI$^+$ ion is larger (1.50 Å) than that of In$^+$ (1.40 Å), the energy needed to go from oxidation state +1 to +III is higher for TI$^+$ than for In$^+$. The sum of the second and third ionizations energies is 4848 kJ mol$^{-1}$ for TI and 4524 kJ mol$^{-1}$ for In, i.e., a difference of about 7%. TI$^+$ is isoelectronic with Hg, and the extra energy needed to remove two more electrons to get to TI$^{3+}$ obviously stems from the relativistic contraction of the 6s orbital. The "inert 6s$^2$ pair," so often encountered but never explained in textbooks, is a relativistic effect.

**Bottom Line**

The influence of relativity on the properties of heavy elements has been well understood for at least 15 years. This knowledge is naturally finding its way into research work on heavy metal chemistry. See for example the works by Schrobgilen et al. (24–26). It is high time that this is also reflected in the teaching of chemistry at the undergraduate level. Take a look at the literature suggested at the end of this article and enjoy the thought-provoking and elegant answers to the seemingly innocent question "Why is mercury liquid?" and other puzzles of the periodic table.

**Acknowledgment**

I wish to thank Pekka Pyykö of the University of Helsinki for many valuable comments on this manuscript. His profound understanding and elegant accounts of relativistic effects in chemistry has been a great stimulation for me.

**Suggested Readings**


**Articles in This Journal**


**Literature Cited**

1. Complete the following table showing the quantum numbers and the number of nodes and nodal planes for some atomic orbitals.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$n$</th>
<th>$l$</th>
<th>number of nodes</th>
<th>number of nodal planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2s</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

2. Derive relationships between the quantum numbers and (a) the number of nodes and (b) the number of nodal planes.

3. Using the relationships derived in Q1, work out the number of nodes and nodal planes for the 3d and 4f orbitals.

4. The shapes of the five 3d orbitals are shown below. Draw the nodal planes on each of the orbitals.

5. Using your answer to Q2, draw the shape of one of the 4f orbitals. [Hint: consider the shapes of the orbitals in the sequence 1s, 2p, 3d and 4f]

6. Briefly explain why the atomic radius increases abruptly from neon to sodium.

7. Calculate the shortest wavelength in the continuous x-ray spectrum emitted from a metal target being struck by 30 keV electrons.
7. (a) Sketch the lobe representations of the $1\sigma$ and $1\sigma^*$ orbitals and a molecular orbital (MO) energy level diagram for $\text{H}_2$.
(b) Use the MO diagram from (a) to complete the bond orders in the table below.
(c) Describe the relationship between, on one hand, the bond length and energy and, on the other hand, the bond order.

<table>
<thead>
<tr>
<th></th>
<th>bond length (Å)</th>
<th>bond energy (kJ mol$^{-1}$)</th>
<th>bond order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>0.74</td>
<td>458</td>
<td>1</td>
</tr>
<tr>
<td>$\text{H}_2^+$</td>
<td>~1.06</td>
<td>~269</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2^-$</td>
<td>~1.22</td>
<td>~150</td>
<td></td>
</tr>
<tr>
<td>$\text{He}_2$</td>
<td>~</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{He}_2^+$</td>
<td>~1.04</td>
<td>~350</td>
<td></td>
</tr>
<tr>
<td>$\text{He}_2^{2+}$</td>
<td>~0.70</td>
<td>~800</td>
<td></td>
</tr>
</tbody>
</table>

Optional.
(a) Read the following article on the antibonding effect.
(b) Why is $\text{He}_2$ less stable than two separate He atoms?
In elementary texts, the combination of two equivalent overlapping atomic orbitals (AOs) to give two molecular orbitals (MOs) is usually represented by diagrams which imply that the antibonding MO is destabilized relative to the free AOs by the same amount of energy as its bonding counterpart is stabilized. Likewise, in the case of two nonequivalent AOs, the antibonding MO is depicted as being destabilized relative to the higher of the two AOs by the same amount as the bonding MO is stabilized relative to the lower of the two AOs. In fact it can easily be shown that in a two-orbital situation the antibonding MO is always more antibonding than its bonding counterpart is bonding. Most authors have demonstrated this antibonding effect in terms of the coefficients of the AOs and their effect on bond orders (1–3); thus for example it can be shown that the bond order in He2 is not simply zero, as implied in the most elementary treatments, thus for example it can be shown that the bond order in He2 is greater than that in the separated atoms. If \( S_{AB} \) is the overlap integral \( \int \phi_A \phi_B \, dt \) and \( H_{AB} = \int \phi_A \phi_B \, dt \). If \( E_1 \) and \( E_2 \) are the energies of the bonding and antibonding MOs \( \psi_1 \) and \( \psi_2 \), respectively, then

\[
[E_2 - E_o(B)] - [E_o(A) - E_1] = -2H_{AB}S_{AB}((1 - S_{AB}) + S_{AB}^2[E_o(A) + E_o(B)] / (1 - S_{AB}))
\]

The right-hand side of eq 4 will be positive if \( 2H_{AB} < S_{AB}E_2 \), as in the homonuclear situation treated in ref 4—that is, the antibonding MO is more antibonding than its bonding counterpart is bonding, as shown in Figure 1. If both are filled, the total orbital energy will be greater than that in the separated atoms. If \( H_{AB} \) is deemed to be proportional to \( S_{AB} \)—as discussed in ref 4—this antibonding effect is proportional to \( S_{AB}^2 \), as in the homonuclear situation treated in ref 4.
Buffering the Antibonding Effect

Suppose that we enlarge the basis set to include AOs lying higher in energy than $\phi_1$ and $\phi_2$, and that one of the additional MOs thus generated, $\psi_3$, has the same symmetry as $\psi_1$. These must be combined to give two new orthogonal MOs $\psi_1'$ and $\psi_2'$, as shown in Figure 2. If in the ground state $\psi_1$ and $\psi_2$ are filled while $\psi_3$ is empty, the antibonding effect—compared with that depicted in Figure 1—will be much reduced, and if the interaction between $\psi_2$ and $\psi_3$ is strong the overall effect may be bonding with respect to the separated atoms. This will apply a fortiori if $\psi_1$ is also depressed in energy by interaction with a higher, empty orbital. Thus the antibonding effect can be buffered by the proximity of such additional orbitals. According to second-order perturbation theory (5), the extent of this buffering will be approximately proportional to $H_{13}^2/(E_3 - E_2)$, or to $S_{13}^2/(E_3 - E_2)$, since $H_{AB}$ is deemed to be approximately proportional to $S_{AB}$.

We now look at some examples of the antibonding effect and its buffering.

Homonuclear Diatomic Molecules

The He$_2$ Molecule

In the case of two He atoms at about the same internuclear distance as in H$_2$ (0.74 Å), the overlap integral between the two 1s orbitals can be calculated from the formula given by Mulliken et al. (6) to be around 0.5, leading to a strong antibonding effect. This is only slightly mitigated by the buffering effect of the 2s and 2p orbitals. The non-orthogonality of $\sigma$ MOs derived from the 1s AOs to those derived from the 2s or 2p orbitals arises from the fact that the $\sigma$ overlap integrals $S(1s,2s)$ and $S(1s,2p)$ are nonzero (7); however, the buffering effect is small on account of the mismatch in size between the compact 1s and diffuse 2s/2p orbitals and because the 2s and 2p orbitals are some 20 eV higher in energy than the 1s orbitals (8). As the internuclear distance increases, the overlap integral falls off sharply; at a distance of 3.0 Å, $S(1s,1s)$ is only 0.003. Since the antibonding effect is approximately proportional to $S^2$, it is now negligible compared with the situation at what might be regarded as a normal bonded distance. Quantum mechanical calculations (9) do in fact lead to a shallow energy minimum at about 3.0 Å, corresponding to a dissociation energy of about 0.1 kJ mol$^{-1}$; elsewhere (10) a dissociation energy of 3.6 kJ mol$^{-1}$ is tabulated for He$_2$. These values indicate a molecule held together very weakly by London forces.

The Be$_2$ Molecule

The “instability” of Be$_2$ can be easily explained in terms of the familiar MO diagram for a homonuclear diatomic molecule of the first short period. The left-hand side of Figure 3 is drawn so as to show the antibonding effect, but without the buffering effect as a consequence of 2s–2p overlap. The right-hand side of Figure 3 shows how the inclusion of 2s–2p overlap alters the picture. The MOs $\sigma_1$ and $\sigma_2$ both have $\sigma^+_g$ symmetry and are non-orthogonal if the 2s and 2p orbitals on different atoms have nonzero overlap (11); their combination yields $\sigma_1$ and $\sigma_3$. Likewise $\sigma^+_1$ and $\sigma^+_2$ both belong to $\sigma^+_g$, and are combined to give $\sigma_4$ and $\sigma_5$. The MO labeled $\sigma_1$ is bonding with respect to 2s–2s, 2p–2p, and 2s–2p overlap; $\sigma_2$ is antibonding with respect to 2s–2s and 2p–2p overlap through mixing between $\sigma^+_1$ and $\sigma^+_2$, but bonding with respect to 2s–2p interaction. The ground state of Be$_2$ arises from the configuration ($\sigma_2$)$^2$$\sigma_1^+$$\sigma_3^+$$\sigma_1^-$, and the stabilization of both filled MOs effectively removes the antibonding effect. Note that the 2p orbitals of Be lie only about 3.4 eV higher in energy than the 2s orbitals, so that 2s–2p interaction will be much more important here than 1s–2p interaction in He$_2$. The dissociation energy of 59 kJ mol$^{-1}$ and internuclear distance of 2.45 Å (12, 13) are consistent with a weak covalent bond of order less than unity.

The F–F and O–O Bonds

The surprisingly low dissociation energy (10) of the F$_2$ molecule (159 kJ mol$^{-1}$) contributes to its high reactivity and to the thermodynamic stability of fluorides. The internuclear distance of 1.42 Å is a little longer than might have been expected: the fluorine atom is usually accorded a covalent radius of 0.64 Å in the tabulations to be found in standard texts (14), rather than 0.71 Å as might be inferred from F$_2$. The usual explanation puts the blame on repulsion between lone pairs. This is analogous to the conventional explanations for the barrier to internal rotation in the ethane molecule (4) and suggests that the antibonding effect might provide an alternative interpretation. The ground state of F$_2$ arises from the configuration ($\sigma_2$)$^2$$\sigma_1^+$$\sigma_3^+$$\sigma_1^-$, and is there a $\sigma$-
antibonding effect, arising from occupancy of \( \sigma_1 \) (which is bonding with respect to 2s–2s and 2p–2p overlap, but antibonding with respect to 2s–2p)? Probably not; the destabilization of \( \sigma_1 \) compared with \( \sigma_0 \) has to be set alongside the stabilization of \( \sigma_1 \) and \( \sigma_2 \), and in any case 2s–2p mixing is likely to be less important in \( \text{F}_2 \) than in \( \text{Be}_2 \) on account of the much larger 2s–2p separation in the F atom (20.9 eV, about the same as the 1s–2p separation in He). However, the filling of \( \pi^* \) will lead to a substantial \( \pi \)-antibonding effect, and this affords an explanation for the weakness of the F–F bond. In the case of \( \text{Cl}_2 \) the \( \pi \)-antibonding effect is much smaller because 3p(\( \pi \))–3p(\( \pi \)) interaction is much weaker than 2p(\( \pi \))–2p(\( \pi \)). The O–O and N–N bonds in molecules such as \( \text{H}_2\text{O}_2 \) and \( \text{N}_2\text{H}_4 \) are comparable in weakness to the F–F bond. This too is usually attributed to repulsions between lone pairs (two on each O atom, one on each N atom). In an MO treatment of \( \text{H}_2\text{O}_2 \) the lone pairs are to be identified with approximately nonbonding MOs, which, however, have appreciable antibonding character. This is most easily shown by performing a qualitative MO treatment by combining the MOs of two OH radicals (cf. the treatment of ethane in ref 4) as shown in Figure 4; for simplicity, the oxygen 2s orbitals are ignored. In OH we have a \( \sigma \)-bonding and a \( \sigma \)-antibonding MO, with a pair of nonbonding orbitals that are pure 2p(O). The \( \text{H}_2\text{O}_2 \) molecule has \( C_2 \) symmetry, with a dihedral angle in the gas phase close to 90°, although in crystalline environments the angle may range up to 180° (15). The \( \text{O}–\text{H} \) bonding MOs 1a and 1b are slightly stabilized relative to the OH radical by interaction with the O–O bonding MO 2a and the “lone pair” orbitals 2b and 3a. But these last three—which are all filled—will be destabilized as a consequence of this interaction, and there will be an overall antibonding effect. The effect on 2b will be buffered to some extent by the O–O antibonding MO 3b and the antibonding effect arises mainly from occupancy of 3a. The magnitude of the antibonding effect is proportional to the square of the overlap integral between the overlapping orbitals on the two OH fragments. Because O is more electronegative than H, in all the occupied MOs the coefficients of O(2p) will be greater than those of 1s(H), and this will enhance the antibonding effect.

Consider now the \( \text{O}_2\text{F}_2 \) molecule. There will now be overlap between the filled “lone pair” orbitals on the O atoms and filled 2p(F) orbitals. The resulting antibonding effect will weaken the O–F bonds. However, because F is more electronegative than O, the coefficients of O(2p) in the occupied MOs will be smaller, thus reducing the overlap integrals that give rise to the antibonding effect between the O atoms. The result is a strengthening of the O–O bond and a concomitant weakening of the O–F bonds, as found experimentally (16), although it must be admitted that the magnitudes of the differences in bond lengths by comparison with \( \text{H}_2\text{O}_2 \) and \( \text{OF}_2 \) are still surprisingly large.

An alternative explanation for the weakness of the F–F bond has been put forward by Politzer (17) and (in a slightly different form) by Sanderson (18). They argue that the small size of the F atom causes large Coulombic repulsion terms between its electrons, which have the effect of lowering its electron affinity and weakening covalent bonds by about 110 kJ mol\(^{-1}\) per F atom. Thus the anomalous properties of the \( \text{F}_2 \) molecule stem from anomalous properties of the fluorine atom. Similar though smaller effects are claimed for O–O and N–N bonds (19). The conventional explanation in terms of repulsions between lone pairs on neighboring atoms can easily be reconciled with the discussion presented here in terms of the antibonding effect—cf. the correspondence between the interpretation of the barrier to internal rotation in ethane in terms of the antibonding effect and in terms of overlap repulsion (4). However, it is less easy to relate the Politzer–Sanderson interpretation to any antibonding effect.

### Stereochemistry of d\(^8\), d\(^9\), and d\(^{10}\) Transition Metal Ions (20)

Where the \( \text{nd} \) subshell is full or nearly full, at least one antibonding MO will usually have to be occupied, and the antibonding effect will dictate that the preferred geometries are those that minimize the number of antibonding electrons and those in which the antibonding effect is most effectively buffered. It may be useful here to distinguish between the obvious primary consequences of the occupation of antibonding MOs, and the secondary antibonding effect that forms the basis for this paper, that is, the enhancement of the primary destabilization as a consequence of the overlap integral terms in normalization coefficients. For example, in an octahedral complex \( \text{MX}_6 \) the ligand field \( e_g(d_{\pi})(d_{\sigma})(d_{\tau}) \) orbitals are, in MO theory, \( \sigma \)-antibonding. There is spectroscopic evidence that the extent of their destabilization for halide ligands is in the order \( \text{F} > \text{Cl} > \text{Br} > \text{I} \), in accordance with the spectrochemical series, but the secondary antibonding effect is expected to be in the reverse sequence, reflecting the covalency in the M–X bond as predicted by simple electronegativity arguments and substantiated by the nephelauxetic effect (21).

#### d\(^8\) Systems

The d\(^8\) configuration is mainly represented among compounds of the 3d series by Co(I), Ni(II), and Cu(III), of which Ni(II) is most familiar. Co(I) compounds are typically trigonal bipyramidal and diamagnetic, with \( \pi \)-acceptor ligands such as CO and PR\(_3\). The highest occupied MOs (HOMOs) have \( e' \) and \( e'' \) symmetry, corresponding to the ligand field \( d_{\pi} \) and \( d_{\sigma} \) orbitals respectively; both are \( \pi \)-bonding in the presence of \( \pi \)-acceptor ligands, although the former is weakly \( \sigma \)-antibonding. The lowest unoccupied MO (LUMO) is \( a_1' \), a \( \sigma \)-antibonding MO that corresponds to the ligand field \( d_{\sigma} \) orbital.

![Figure 4. MOs of \( \text{H}_2\text{O}_2 \), constructed from two OH radicals.](Image)
Ni(II) complexes may be octahedral, trigonal bipyramidal, square pyramidal, square planar, or tetrahedral. The factors that govern the preferred geometry for a given ligand set have been much discussed in terms of ligand field and steric arguments, but the antibonding effect needs to be considered too. In an octahedral $d^6$ complex, the HOMO is the $\sigma$-antibonding degenerate pair $e_g$, the $d_{xy},d_{xz},d_{yz}$ ligand field orbitals. Although this is only half-filled, the antibonding effect ensures that the destabilization may be greater than expected, and there may be some tendency to shed one or two ligands to give diamagnetic trigonal bipyramidal or square planar species, respectively; the latter tendency will be discussed in more detail when we look at Jahn–Teller distortions in $d^9$ systems. It must be remembered that in, for example, a nickel(II) complex, the metal 4$s$ and 4$p$ orbitals are at least as much engaged in covalent bonding as the $d$ orbitals; and a lowering of the coordination number, which might render the ligand field $e_g$ orbitals less antibonding, will necessarily destabilize bonding MOs involving 4$s$ and 4$p$ as well as $d$. The antibonding effect discussed in this paper may well be decisive in such situations. The greater the degree of covalency in the metal–ligand bond—that is, the larger the overlap integral $S$—the greater will be the antibonding effect and hence the greater will be the preference for lower coordination numbers. Thus with soft ligands having donor atoms of low electronegativity (CN$^-$, PR$_3$, etc.) Ni(II) complexes are mostly square planar or trigonal bipyramidal, and diamagnetic. Pd(II) and Pt(II) are considerably softer than Ni(II), and their complexes are almost all square planar, as are those of Ag(III) and Au(III). Apart from Ni(II), the majority of paramagnetic, octahedral $d^8$ species are fluorides and fluorocomplexes such as PdF$_2$ and AgF$_6^{3-}$, where the (secondary) antibonding effect is expected to be small.

$d^9$ Systems

These are mostly represented by Cu(II). With three electrons in the $e_g$ level, the antibonding effect for octahedral Cu(II) is stronger than for octahedral Ni(II), and the former will be more unstable with respect to chemical changes that will mitigate the effect. The so-called Jahn–Teller distortion, the removal of two axial ligands to give axially elongated octahedral and ultimately square planar geometry, is an example of such a change.

Figure 5 shows the effects on the MOs of an octahedral complex (considering only $\sigma$-bonding) of removing two opposite ligands to the point that they are no longer effectively bonded; the diagram on the right-hand side of Figure 5 represents a square planar complex, with nonbonding axial ligand orbitals deleted. Axially elongated “$4 + 2$” coordination and square pyramidal 5-coordination are intermediate cases. The removal of two ligands allows the remaining four to approach the central atom a little closer, on account of the reduction in inter-ligand repulsion. This accounts for the slight stabilization of square planar $1e_g$ compared with octahedral $1t_{2u}$, and the destabilization of the antibonding $2e_u$. It also accounts for the stabilization and destabilization respectively of $1b_{1g}$ and $2b_{1g}$. With only four instead of six ligands, the octahedral $1a_{1g}$ and $2a_{1g}$ become less bonding and antibonding, respectively.

But the most dramatic feature of Figure 5 is the stabilization of the square planar $2a_{1g}$ (i.e., the ligand field $d_{xy}$ orbital) relative to the octahedral $2e_u$. In the angular overlap model (21, 22), the destabilization of $d_{xy}$ in an octahedral complex is expressed as $\Delta E_{d_{xy}} = \epsilon_{d_{xy}} - \epsilon_{d_{eq}}$, where $\epsilon_{d_{eq}}$ denotes the two axial ligands on the $z$ axis and $\epsilon_{d_{ax}}$ denotes the four equatorial ligands in the $xy$ plane. With the removal of the two axial ligands, the axial antibonding effect disappears, whereas the weaker equatorial antibonding effect is buffered by interaction between $2a_{1g}$ and $3a_{1g}$ as the axial ligands are withdrawn.

Ligand field treatments of the $d$–$d$ spectra of square planar complexes (21–23) lead to the conclusion that in square planar complexes the $d_{xy}$ orbital lies lowest in energy; this can only be explained within the angular overlap model by invoking $nd-(n+1)s$ mixing, with the introduction of a new parameter, $\epsilon_{d_{eq}}$ (21, 22, 24), although the cellular ligand field approach (23) can account for this observation without explicit d–s mixing. In the $d$–$d$ spectra of square planar Cu(II) complexes, the $d_{xy} \rightarrow d_{xy}$ transition is usually found in the region 16,000–20,000 cm$^{-1}$ (21–24), which corresponds to about 200 kJ mol$^{-1}$, comparable to a metal–ligand bond energy. Thus the stabilization of $2a_{1g}$ in square planar complexes provides the driving force for the Jahn–Teller effect; the extent of this stabilization as the axial ligands are withdrawn results from a combination of the diminished primary destabilization, the overlap-dominated antibonding effect, and the buffering effect of the 4$s$ orbital on the residual antibonding effect in the “$4 + 2$” and square-pyramidal configurations. Note that an axial compression, as opposed to an elongation, would also satisfy the Jahn–Teller theorem, but is very rarely observed. Such a distortion from octahedral geometry leads to much less stabilization because $2a_{1g}$ is now singly occupied while $1b_{1g}$ is filled (25); the antibonding effect is much greater, and is less effectively buffered than for the axially elongated configuration.

$d^{10}$ Systems

We look first at Zn(II), which has a distinct preference for tetrahedral coordination. Thus although Zn$^{2+}$ and Mg$^{2+}$ are very similar in size, Mg(II) in binary compounds MgO, MgS, and MgX$_2$ ($X$ = halogen) has octahedral coordination, whereas the zinc analogues prefer tetrahedral coordination except in ZnF$_2$. Zn(II) is also found in tetrahedral coordination in metalloenzymes such as carboxypeptidase A, alcohol dehydrogenase, carbonic anhydrase, and superoxide dismutase, although it can increase its coordination number to five. In an octahedral $d^{10}$ system, the $2e_u$ level in Figure 5 is filled, causing
a severe antibonding effect, which explains why octahedral Zn(II) complexes are relatively scarce.

Why does Zn(II) prefer tetrahedral coordination? Square planar coordination would entail double occupancy of 2b_{1g} with a strong antibonding effect. The HOMO in a tetrahedral d^{10} system corresponds to the ligand field t_{2g} level, which is \sigma-antibonding as far as overlap between the metal 3d orbitals and the ligand orbitals are concerned. However, in tetrahedral symmetry the metal 4p orbitals are also t_{2g}, so that there lies above the HOMO another t_{2g} MO, which is antibonding with respect to overlap involving the 4p AOs. Interaction between these two has the effect of buffering the lower, filled t_{2g} MO, which is now \sigma-bonding with respect to overlap between the metal 4p orbitals and ligand orbitals. This 3d–4p mixing in tetrahedral complexes manifests itself in the higher intensities of d–d bands in tetrahedral compared with octahedral complexes (21), and in the quantitative interpretation of d–d transition energies in distorted tetrahedral CuCl_{4}^{2−} (24). Cu(I) is most often found in tetrahedral coordination, but it has practically no tendency to adopt five- or six-coordination, and, unlike Zn(II), is often found in trigonal three- or linear two-coordination. In these lower coordination numbers, the HOMO is the ligand field d_{z^2} orbital, which—as in square planar geometry—has the same symmetry as 4s. Thus the antibonding effect in the HOMO is buffered by 3d–4s mixing. This 3d–4p mixing is not necessarily more effective for Cu(I) than for Zn(II); it is more important because Cu(I) is generally acknowledged (26) to be “soft”, whereas Zn(II) is classified as “borderline”, implying greater covalency and greater overlap for Cu(I) complexes, which enhances the antibonding effect. These lower coordination geometries are also common for other soft d^{10} species such as Pd(O), Pt(O), Ag(I), Au(I), and Hg(II).

Literature Cited

16. Ibid., p. 638.
20. The relevant chapters of Greenwood, N. N.; Earnshaw, A. (op. cit.) contain all the factual material relied upon in this section.
1. The molecular orbital diagram for \( \text{O}_2 \) is shown on the right.

(a) Write out the (valence) electron configuration.

(b) Complete the table below by calculating bond orders for \( \text{O}_2 \) and its ions and use these values to explain the observed variation in bond length.

<table>
<thead>
<tr>
<th>bond order</th>
<th>bond length / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>1.21</td>
</tr>
<tr>
<td>( \text{O}_2^+ )</td>
<td>1.12</td>
</tr>
<tr>
<td>( \text{O}_2^- )</td>
<td>1.34</td>
</tr>
<tr>
<td>( \text{O}_2^{2-} )</td>
<td>1.49</td>
</tr>
</tbody>
</table>

2. For all of the homonuclear diatomics \( \text{X}_2 \) of the second period (\( \text{X} = \text{Li} - \text{Ne} \)), determine the change in bond order and, hence, the change in bond length due to (i) removing an electron to form \( \text{X}_2^+ \) and (ii) adding an electron to form \( \text{X}_2^- \). (Use the MO diagram for \( \text{O}_2 \) provided in Q1).

3. On the basis of ionic radii, predict whether \( \text{NaBr} \) will have the same crystal structure as \( \text{NaCl} \) or \( \text{CsCl} \).

4. Sketch a unit cell (one complete cube) of an fcc lattice.

5. \( \text{CdS} \) is a semiconductor that absorbs in wavelengths below about 470 nm. Calculate its band gap in joules. What colour do you expect it to be?

6. Starting from the \( \text{NaCl} \) unit cell, calculate the density of table salt. The ionic radii for \( \text{Na}^+ \) and \( \text{Cl}^- \) are 1.02 and 1.81 Å respectively.

(Hint: density = mass / volume and so you need to calculate the mass and the volume of the unit cell. When calculating the mass, remember that ions on corners, edges and faces are shared with other cells so that only a fraction of their mass contributes. When calculating the volume, remember that the ions are closed packed).
1. Draw out plausible Lewis structures for the following species, *including* resonance structures if appropriate.

   (a) hydrogen cyanide, HCN. What is the C–N bond order from the Lewis model?
   (b) ethanol, CH₃CH₂OH. How many lone pairs are on the oxygen?
   (c) pyridine, C₅H₅N. (Pyridine is a six-membered ring like benzene, but one of the carbons is replaced by a nitrogen.)
   (d) acetylene, C₂H₂. How many π-bonds in this molecule?
   (e) SOCl₂
   (f) N₂O₄
   (g) phosphoric acid, H₃PO₄ [=PO(OH)₃]
   (h) phosphate anion, PO₄³⁻. What is the average P–O bond order from the resonance structures?
   (i) methylsulfate anion, CH₃OSO₃⁻

2. Using Lewis theory and VESPR theory, predict the shapes of the following molecules and ions.

   (a) NO₃⁻  (b) H₃O⁺  (c) O₃  (d) SF₆
   (e) PF₅  (f) SF₄  (g) ClF₃  (h) XeF₂

3. What are the approximate bond angles at the atoms indicated by the arrows in each of the following compounds?

   (a) CH₃–C–H
   (b) CH₃–C–OH
   (c) CH₃–C–OH
   (d) CH₃–C–O–CH₃
   (e) CH₃–C≡C–H
   (f) CH₃–C≡C–H

4. What are the approximate bond angles in adrenaline at the atoms indicated by the arrows?
1. The temperature of the sun is 5800 K and its radius is 696000 km. Using the Stefan-Boltzmann equation, verify that the power density at the Earth’s surface, \(1.50 \times 10^8\) km from the sun is 1370 J s\(^{-1}\) m\(^{-2}\).

2. Venus is \(1.09 \times 10^8\) km from the sun. Estimate the temperature of Venus in the absence of any greenhouse effect using its experimental albedo of 65%.

3. The star Betelgeuse has a surface temperature of approximately 3400 °C.
   (a) Estimate the wavelength of its maximum emission
   (b) Calculate the wavenumber corresponding to that wavelength.

4. A mixture of gases at 1.00 atm contains 55.0% nitrogen, 25.0% oxygen and 20.0% carbon dioxide by volume. What is the partial pressure of each gas?

5. The molar heat capacities of Cl\(_2\)(g) and liquid water are approximately 37.0 and 75.3 J K\(^{-1}\) mol\(^{-1}\) respectively. If 1 kJ of energy were used to heat 1 mole of each of liquid water and chlorine gas initially at 25 °C, which would become hotter? How much hotter?

6. 100 mL of 1.0 M HCl and 100 mL of 1.0 M NaOH, both at 24.6 °C, are mixed in a calorimeter. After the reaction, the temperature was 31.3 °C. Assuming that the heat capacity of the calorimeter is negligible, and approximating the heat capacity of the solution by that of water, calculate the standard enthalpy of reaction for the neutralisation of H\(^{+}\)(aq) by OH\(^{-}\)(aq).

7. Diborane (B\(_2\)H\(_6\)) is a highly reactive gas at room temperature and pressure and was once considered as a possible rocket fuel for the US space program. Calculate the heat of formation of diborane from the following data.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B(s) + (\frac{3}{2})O(_2)(g) (\rightarrow) B(_2)O(_3)(s)</td>
<td>-1273</td>
</tr>
<tr>
<td>B(_2)H(_6)(g) + 3O(_2)(g) (\rightarrow) B(_2)O(_3)(s) + 3H(_2)O(g)</td>
<td>-2035</td>
</tr>
<tr>
<td>H(_2)(g) + (\frac{1}{2})O(_2)(g) (\rightarrow) H(_2)O(l)</td>
<td>-286</td>
</tr>
<tr>
<td>H(_2)O(l) (\rightarrow) H(_2)O(g)</td>
<td>+44</td>
</tr>
</tbody>
</table>

8. Write an equation for the combustion of butane gas (C\(_4\)H\(_{10}\)) that produces water vapour.
   (a) Using the ideal gas equation, calculate the change in volume when one mole of butane undergoes complete combustion with a stoichiometric amount of oxygen, at constant pressure (1 atm) and temperature (350 K), and hence determine the work done by the reaction under these conditions.
   (b) Using the definition of enthalpy, generalise your result and propose a formula for the difference between \(\Delta H\) and \(\Delta E\) based on the stoichiometry of any gas phase reaction at constant pressure and temperature.
1. Methyl stearate, CH₃(CH₂)₁₆COOCH₃, is a significant component of some biodiesel formulations. Its heat of formation is –945.6 kJ mol⁻¹.

(a) Calculate its heat of combustion using the standard heats of formation in the table above.

(b) Estimate its heat of combustion from the atomisation energies (using bond enthalpies) of the reactants and products.

(c) Convert your accurate heat of combustion into a nett calorific value (kJ g⁻¹) and compare this with the value for conventional diesel of 42.5 kJ g⁻¹.

2. Answer the following using the data below.

(a) Calculate the entropy and enthalpy change for a reaction in which NO(g) is formed from N₂(g) and O₂(g).

(b) Use these results to write the entropy change of the universe for this reaction as a function of temperature, and hence predict the temperature range in which this reaction will be spontaneous.

3. RDX (C₃H₆N₆O₆) is a powerful explosive.

(a) Write a balanced chemical equation to describe the complete combustion of RDX to give water vapour, carbon dioxide and dinitrogen.

(b) How might the equation for the explosive decomposition of RDX differ from the above equation? Suggest a reasonable chemical equation to describe the overall chemistry.

(c) What properties of RDX make it a good explosive?

(d) How much heat is generated from the complete combustion of 100 g of RDX? Compare this value with the heat generated from explosive decomposition.
4. Using thermochemical data, estimate the longest wavelength that could be used to photolyse CO$_2$(g) into CO(g) + O(g). On this basis, predict whether CO$_2$ in the troposphere will be photolysed.

5. When ammonium nitrite, NH$_4$NO$_2$, is heated, it decomposes to nitrogen gas and water.
   (a) Calculate the heat released by the decomposition of 1.00 g of solid NH$_4$NO$_2$.
   (b) If the reaction were carried out at 1 atm pressure and 250 °C, calculate the volume of gas generated by this reaction.
   (c) Calculate the temperature increase in the reaction mixture if the reaction were carried out in an insulated container of fixed volume (a bomb calorimeter). Neglect the heat capacity of the container.

\[ C_V = 21 \text{ J K}^{-1} \text{ mol}^{-1} \text{ for N}_2 \text{ and } 26 \text{ J K}^{-1} \text{ mol}^{-1} \text{ for H}_2\text{O}. \]

6. In the reaction \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g), \quad K_c = 4.35 \text{ M}^{-1} \text{ at } 600 \degree \text{C}. \] The three gases are injected into a vessel such that their concentrations are \([\text{SO}_2] = 2.00 \text{ M}, \quad [\text{O}_2] = 1.50 \text{ M} \text{ and } [\text{SO}_3] = 3.00 \text{ M}. \] Are the gases in the vessel at equilibrium initially? If not, in which direction will the reaction proceed?
1. Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations if a 1.000 L flask is charged with 1.000 mol of each gas at 700 K.

2. Ammonium carbamate (NH$_2$CO$_2$NH$_4$) is a salt of carboxamic acid that is found in the blood and urine of mammals. At 250 °C, $K_c = 1.58 \times 10^{-8}$ for the following equilibrium:

$$\text{NH}_2\text{CO}_2\text{NH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$$

If 7.80 g of NH$_2$CO$_2$NH$_4$ is introduced into a 0.500 L evacuated container, what is the total pressure inside the container at equilibrium at 250 °C?

4. SO$_3$ is produced from the reaction SO$_2$(g) + $\frac{1}{2}$O$_2$(g) $\rightleftharpoons$ SO$_3$(g), for which $\Delta H^\circ = -99$ kJ mol$^{-1}$ and $K_c = 1.3 \times 10^4$ at 600 K.

(a) What can be done, industrially, to improve the yield of SO$_3$?
(b) Explain why a catalyst is used in the industrial production of SO$_3$.
(c) At equilibrium, $p$(SO$_3$) = 300 atm and $p$(O$_2$) = 100 atm. Calculate $p$(SO$_2$).
(d) The engineer places a mixture of 0.0040 mol SO$_2$(g) and 0.0028 mol O$_2$(g) in a 1.0 L container and raises the temperature to 1000 K. At equilibrium, 0.0020 mol SO$_3$(g) is present. Calculate $K_c$ and $p$(SO$_2$) for this reaction at 1000 K.

5. The equilibrium constants for the formation of MnO, CO$_2$ and CO from their constituent elements as a function of temperature (in K) are shown below.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K$(CO)</th>
<th>$K$(MnO)</th>
<th>$K$(CO$_2$)</th>
<th>$T$ (K)</th>
<th>$K$(CO)</th>
<th>$K$(MnO)</th>
<th>$K$(CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.01 x 10$^{34}$</td>
<td>1.40 x 10$^{63}$</td>
<td>1.96 x 10$^{34}$</td>
<td>875</td>
<td>2.00 x 10$^{11}$</td>
<td>1.24 x 10$^{19}$</td>
<td>6.44 x 10$^{11}$</td>
</tr>
<tr>
<td>400</td>
<td>1.48 x 10$^{19}$</td>
<td>2.43 x 10$^{46}$</td>
<td>5.49 x 10$^{25}$</td>
<td>1000</td>
<td>2.97 x 10$^{10}$</td>
<td>1.66 x 10$^{16}$</td>
<td>2.20 x 10$^{10}$</td>
</tr>
<tr>
<td>500</td>
<td>1.87 x 10$^{16}$</td>
<td>2.14 x 10$^{36}$</td>
<td>4.05 x 10$^{20}$</td>
<td>1250</td>
<td>2.06 x 10$^{9}$</td>
<td>1.57 x 10$^{12}$</td>
<td>1.95 x 10$^{08}$</td>
</tr>
<tr>
<td>625</td>
<td>8.96 x 10$^{13}$</td>
<td>1.93 x 10$^{28}$</td>
<td>3.17 x 10$^{16}$</td>
<td>1500</td>
<td>3.47 x 10$^{8}$</td>
<td>3.28 x 10$^{9}$</td>
<td>8.34 x 10$^{6}$</td>
</tr>
<tr>
<td>750</td>
<td>2.55 x 10$^{12}$</td>
<td>8.38 x 10$^{22}$</td>
<td>5.81 x 10$^{13}$</td>
<td>1750</td>
<td>9.74 x 10$^{7}$</td>
<td>3.98 x 10$^{7}$</td>
<td>8.79 x 10$^{5}$</td>
</tr>
</tbody>
</table>

(a) Write the chemical equations that describe the formation reactions of these compounds, together with their equilibrium constant expressions. Each equation should be written to consume 1 mole of oxygen atoms.
(b) Construct an Ellingham diagram (ln $K$ versus $T$) for MnO, CO$_2$ and CO and determine the conditions under which (i) carbon dioxide and carbon monoxide are the preferred products, and (ii) manganese metal can be won from the ore by smelting with coke, and identify which oxide of carbon is the by-product.
(c) The standard enthalpy and entropy change for coke smelting of MnO are +274 kJ mol$^{-1}$ and 164 J K$^{-1}$ mol$^{-1}$, respectively. Calculate the temperature range in which the production of metallic manganese will be spontaneous under standard conditions.
1. Write half-cell and balanced overall cell reactions for the electrochemical cells given below in standard notation. Using the data in the table of reduction potentials, calculate \( E^\circ \) for each reaction, and identify the oxidant and reductant.

   (a)  \( \text{Al(s)} | \text{Al}^{3+}(aq) \ || \text{Sn}^{2+}(aq) | \text{Sn(s)} \)
   (b)  \( \text{Pt(s)} | \text{Fe}^{2+}(aq), \text{Fe}^{3+}(aq) \ || \text{Ag}^+(aq) | \text{Ag(s)} \)
   (c)  \( \text{Pt(s)} | \text{MnO}_4^-(aq), \text{H}^+(aq), \text{Mn}^{2+}(aq) \ || \text{Sn}^{4+}(aq), \text{Sn}^{2+}(aq) | \text{Pt(s)} \)

2. Use the table of reduction potentials to predict whether, to any significant extent

   (a) \( \text{Mg(s)} \) will displace \( \text{Pb}^{2+} \) from aqueous solution
   (b) Tin will react and dissolve in 1 M HCl
   (c) \( \text{SO}_4^{2-} \) will oxidise \( \text{Sn}^{2+} \) to \( \text{Sn}^{4+} \) in acidic solution
   (d) \( \text{MnO}_4^- \) will oxidise \( \text{H}_2\text{O}_2(aq) \) to \( \text{O}_2(g) \) in acidic solution

3. Write the equilibrium constant expression for each of the following reactions, and determine the value of \( K \). Use the data from the standard reduction potential table.

   (a)  \( \text{Sn}^{2+}(aq) + 2\text{Ag}^+(aq) \rightleftharpoons \text{Sn}^{4+}(aq) + 2\text{Ag}(s) \)
   (b)  \( \text{MnO}_2(s) + 4\text{H}^+(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}(l) + \text{Cl}_2(g) \)

4. Use the Nernst Equation and the table of standard reduction potentials to calculate \( E_{\text{cell}} \)

   for each of the following cells.

   (a)  \( \text{Al(s)} | \text{Al}^{3+} \) (0.18 M) || \( \text{Fe}^{2+} \) (0.85 M) | \text{Fe(s)}
   (b)  \( \text{Ag(s)} | \text{Ag}^+ \) (0.34 M) || \( \text{Cl}_2(g, 0.55 \text{ atm}) \) | \( \text{Cl}^- \) (0.098 M) | \text{Pt(s)}

5. For each of the following combinations of electrodes and solutions, indicate:

   (i) The overall cell reaction;
   (ii) Which electrode is the anode and which is the cathode;
   (iii) The direction in which electrons flow spontaneously;
   (iv) The magnitude of the initial voltage.

<table>
<thead>
<tr>
<th>Electrode A</th>
<th>Solution A</th>
<th>Solution B</th>
<th>Electrode B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Cu</td>
<td>1.0 M ( \text{Cu}^{2+} )</td>
<td>1.0 M ( \text{Fe}^{2+} )</td>
<td>Fe</td>
</tr>
<tr>
<td>(b) Pt</td>
<td>1.0 M ( \text{Sn}^{2+} / 1.0 \text{ M Sn}^{4+} )</td>
<td>1.0 M ( \text{Ag}^+ )</td>
<td>Ag</td>
</tr>
<tr>
<td>(c) Zn</td>
<td>0.1 M ( \text{Zn}^{2+} )</td>
<td>1.0 ( \times 10^{-3} ) M ( \text{Fe}^{2+} )</td>
<td>Fe</td>
</tr>
</tbody>
</table>

6. Magnesium metal is produced by the electrolysis of molten magnesium chloride. Sketch the cell and label the anode and cathode. Indicate the direction of electron flow through the wire. What are the oxidation and reduction half-reactions?

7. How many hours are required to produce 1000 kg of chlorine gas by the electrolysis of an aqueous NaCl solution with a constant current of \( 3 \times 10^4 \) A? What volume (in litres) is occupied by this amount of chlorine at 1 atm pressure and 298 K?
8. The dipole moments and boiling points of CH$_2$F$_2$, CH$_2$Cl$_2$ and CH$_2$Br$_2$ are listed in the table below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH$_2$F$_2$</th>
<th>CH$_2$Cl$_2$</th>
<th>CH$_2$Br$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole moment, µ (D)</td>
<td>1.93</td>
<td>1.60</td>
<td>1.43</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-52</td>
<td>41</td>
<td>99</td>
</tr>
</tbody>
</table>

(a) What intermolecular forces operate in these compounds?
(b) Briefly explain why the boiling points increase in the order CH$_2$F$_2$ < CH$_2$Cl$_2$ < CH$_2$Br$_2$.

9. The structure of the hormone adrenaline is shown below. For each of the areas A, B, C and D indicate the types of intermolecular interaction likely to be important in binding the hormone to a receptor.