

Why Is Mercury a Liquid?

The silver liquid called mercury has been known since ancient times. In fact the symbol for mercury (Hg) comes from its Greek name *Hydrargyrum*, which means watery silver. Although elements in the liquid state at ambient temperature and pressure are quite rare (Br₂ is another example), the liquid nature of mercury is especially confounding. For example, compare the properties of mercury and gold:

	Mercury	Gold
Melting point	-39°C	1064°C
Density	13.6 g cm ⁻³	19.3 g cm ⁻³
Enthalpy of fusion	2.30 kJ mol ⁻¹	12.8 kJ mol ⁻¹
Conductivity	10.4 kS m ⁻¹	426 kS m ⁻¹

It is quite apparent that these metals, which are neighbors on the periodic table, have strikingly different properties. Why? The answer is not at all straightforward—but very interesting. It seems to hinge on relativity.

Recall that Einstein postulated in his theory of special relativity in 1905 that the mass (m) of a moving object increases with its velocity (v):

$$m_{\text{relativistic}} = m_{\text{rest}} \sqrt{1 - (v/c)^2}$$

where c is the speed of light. In the simple models for the atom we ignore relativistic effects on the electron mass. Although these effects are negligible for light atoms (the mass change is approximately 0.003% for the hydrogen electron), they become important for heavy elements such as gold and mercury. For example, the relativistic mass for a 1s elec-



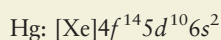
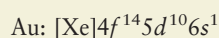
Liquid mercury forms flat drops because of its lack of surface tension.

tron in mercury is approximately 1.23 times its rest mass and this effect leads to a very significant contraction in the radius of the 1s orbital.

It turns out that relativity has an even more profound impact on atomic theory than the above calculations suggest. A relativistic treatment of the atom fundamentally changes the way we view the electrons in atoms. In fact, as shown by British physicist Paul Dirac, the concept of electron spin occurs naturally in a relativistic treatment of the

atom and does not have to be “tacked on” as in the wave mechanical treatment. The point here is not to explain these very complex ideas, but to alert you to concepts you will be learning more about in higher-level courses.

How does relativity explain why mercury has a melting point of -39°C while that of neighboring gold is 1064°C ? The first step in answering this question involves considering the electron configurations of these atoms:



Notice that gold has an unfilled $6s$ subshell but the $6s$ level is filled in mercury. Because of its configuration a gold atom can use its half-filled $6s$ orbital to form a bond to another gold atom. In fact the metal–metal bond in the Au_2 molecule is an astonishingly strong 221 kJ mol^{-1} , a value very close to the bond energy of the Cl_2 molecule (239 kJ mol^{-1}) and greater than the bond energy of I_2 (149 kJ mol^{-1}). In addition, gold has an electron affinity (-220 kJ mol^{-1}) that is higher than that of oxygen and sulfur. Further, gold forms a compound with cesium (CsAu) that exhibits the CsCl crystal structure (see Figure 16.41 and Section 16.8) in which gold atoms take the place of Cl^- ions. Thus a gold atom seems to behave a lot like a halogen atom.

What causes gold to emulate many properties of the nonmetallic halogens? The apparent answer lies in the dramatic contraction of the gold $6s$ orbital because of relativistic effects. The unexpectedly small radius of the $6s$ orbital of a gold atom results in a

much lower energy than is predicted in the absence of relativistic effects. It is this very-low-energy unfilled $6s$ orbital that causes gold atoms to form very stable Au_2 molecules in the gas phase and to bind strongly to each other in the solid state, producing its high melting point. This same low-energy $6s$ orbital also leads to gold’s unexpectedly high electron affinity and to its unusual color. Gold is not the silvery color exhibited by most metals because of the absorption of blue light to transfer an electron between the $5d$ and $6s$ orbitals in gold atoms.

So why are gold and mercury so different? The answer lies in the different electron configurations of the two atoms. Unlike gold, the low-energy $6s$ orbital in mercury is filled and these two electrons are very tightly bound to the mercury atom. In fact, one can think of Hg as being analogous to He. That is, the low-energy pair of $6s$ electrons on mercury causes it to behave like a noble gas atom—it cannot bond to another mercury atom. This explains why mercury is unique among metals in that it is almost entirely monomeric in its gas phase. In contrast, the species Hg_2^{2+} is extremely stable even in aqueous solution. This fact is not surprising once it is realized that Hg^+ is isoelectronic with Au.

Thus it is the unusually low energy of the $6s$ orbitals apparently caused by relativistic effects that causes gold to behave like a halogen atom and mercury to behave like a noble gas. ■

Suggested Reading

Lars J. Norrby, “Why Is Mercury Liquid?”, *J. Chem. Ed.*, **68** (1991): 110.