

By Christen Brownlee

he old-style Volkswagen Beetle: Is it a classic car, or an endangered species? The answer depends on where you live. Although there are few classic cars hanging around the northern states or on the coastlines, plenty of vintage automobiles still exist in the mild southern climates and in America's interior states.

The reason that Volkswagen Bugs and other older cars are dropping like flies isn't the typical habitat loss or human encroachment that's plaguing other endangered species. Classic car fleets are constantly shrinking due to a chemical reaction that you're no doubt already familiar with: rusting.

But why does rust unequally strike cars in the snowy states and coastal towns but leave vehicles elsewhere virtually untouched? And more importantly, how can you keep your beloved grocery-getter safe, no matter

what parking place you call home? Read on to get the lowdown on how rust works and what measures you can take to stop corrosion in its tracks.

Electron swap meet

Like all types of corrosion, rust is actually a chemical bargain, with two reactions in one: reduction, in which some atoms gain electrons, and oxidation, in which other atoms lose electrons. With all those electrons flowing from one place to another, rust-making is also considered an electrochemical reaction. According to John Scully, a



corrosion expert at the University of Virginia in Charlottesville, the redox reaction that forms rust needs just three ingredients to take place: an anode, or metal that readily gives up electrons; a cathode, or substance (in this case, oxygen) that easily accepts electrons; and an electrolyte solution, which shuttles ions between cathode and anode.

Most cars are made mostly of steel, a tough mixture of iron, carbon, and small amounts of other ingredients like manganese, silicon, phosphorus, and sulfur. It's the iron part of steel that corrodes to make rust.

Iron doesn't hold onto its electrons very tightly, says Scully, making it the perfect anode for an electrochemical reaction to take place. Other metal atoms in the steel mixture, or even another point on the piece of iron, make excellent cathodes. Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These defects create anodic regions where the iron is more easily oxidized than it is at others (cathodic regions). However, without a bridge to connect potential anodes and cathodes, rusting would be such a time-consuming process that cars would virtually last forever.

The water on the steel surface is a solvent for ions produced when the iron metal at the anodic region loses electrons (is oxidized to form ferrous ions) and the electrons are conducted through the metal to the cathodic region where they react with water and oxygen from the air to form hydroxide ions, as shown in these equations:

2Fe → 2Fe²⁺ + 4
$$e^-$$
 (oxidation at anodic sites)
4 e^- + 0₂ + 2H₂0 → 40H⁻
(reduction at cathodic sites)

The ions in this electrolyte solution can migrate together and react to form ferrous hydroxide, which reacts further with oxygen from the air to oxidize the ferrous ion and form insoluble ferric oxide, the chemical name for rust, as shown in these equations:

$$Fe^{2+} + 20H^{-} \rightarrow Fe(0H)_{2}$$
 (formation of ferrous hydroxide)

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O$$
 (oxidation to ferric oxide or red 'rust')

The movement of ions through the electrolyte solution completes the electric circuit that allows the electrons from iron to move from the anode to the cathode.



A redox reaction on wheels. The bumper of this vehicle wears the product of the reaction between iron and oxygen—rust!

But all this still doesn't explain why colder climates and coastal areas get an unfair share of rust. The magic ingredient that both areas share—which is missing in the basic recipe for rust—is a high abundance of salt. Coastal areas have plenty of salt sailing through the air from ocean spray, and with each cold, snowy winter, northern states smear tons of rock salt on roads to lower the freezing point of water and help keep roads free or ice and snow. [See "Salting Roads: The Solution for Winter Driving" in this issue]

Salt speeds rust's redox reaction along by making water a better conductor. "Salt allows the anode and cathode to be in touch even better," says Scully, making corrosion happen even quicker. Also, chloride ions form very stable complex ions with Fe³⁺, which helps dissolve iron and accelerate corrosion.

Costly corrosion

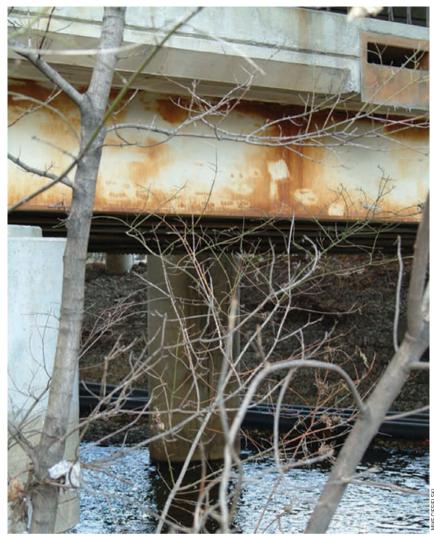
Scully points out that iron can't help rusting—existing as an oxide in its thermodynamically favored state. In fact, the metal rarely exists in a pure state in nature. Before it becomes a side panel in your car, engineers must convert rusty iron ore into a pure metal.

With rust being iron's favored state, it is of little use trying to fix rust after it has already happened. By putting energy into rust, it's possible to plate metal back onto a

car, says Scully. However, it's also incredibly costly and impractical. Plus, by the time most car owners notice a rust spot, a significant amount of iron has already sloughed off of the car, lost to wind and rain.

One solution to stopping iron's thermodynamic conversion, says Scully, would be to make cars out of a metal that doesn't corrode, such as gold or silver. "Converting to an oxide isn't thermodynamically favorable





It's not only cars that are rusting away. Corrosion costs the United States a whopping \$276 billion per year!



reaction for these metals, so they won't corrode spontaneously," he says. "Archaeologists can dig up gold coins that have survived through the ages without corroding."

But while driving a gold car might make you feel like a million bucks, making such a vehicle would cost substantially more. Not to mention the fact that these soft metals would be unable to support the car's weight and would squash like putty in a collision!

Even using noncorroding metals that are cheaper than gold or silver, such as stainless steel that Deloreans are made of, is still more expensive than using the plain steel that most cars are made of today.

The best way to prevent corrosion is still the cheapest. A good coating of paint removes the connection between anode and cathode by preventing water from making contact with steel. Without water, rusting slows down to a snail's pace.



This student investigates the role of salt on the rate of rusting by putting nails in various salt water solutions

Today's high tech paints have evolved far from being just a simple barrier, says Scully. Researchers are currently working on paints that release rust inhibitors on demand when paint's seal on steel is breached, for example, when the paint on a car is scraped or scratched. Other "smart paints" that ooze together to close gaps whenever a car's panels get scratched are also in the works.

Although rust is a big deal for car owners, it's an even bigger deal for industries that rely on machines with metal parts, ranging from farm tools to factory equipment to fighter jets. According to Scully, corrosion costs the United States a whopping annual toll of about \$276 billion in lost goods and services. With the exorbitant cost of new military equipment, the Department of Defense (DOD) is one of the largest investors in antirust research, says Scully. Scientists at the DOD hope they can keep the aging Blackhawk helicopters and B52 bombers that are currently in use running smoothly for decades to come—a cost savings of millions of dollars per machine.

But one military asset sometimes harmed by corrosion is extremely difficult to put a price on, says Scully. "If a soldier goes to war and the rifle he's using to protect himself doesn't fire when he needs it to, how do you estimate the cost of corrosion then?"

Christen Brownlee is a contributing editor to ChemMatters. Her article "Super Fibers" also appears in this issue.