

The Say of Things

BY ROALD HOFFMANN
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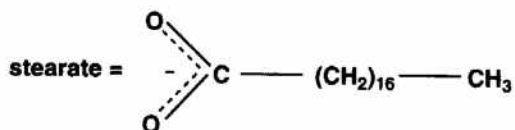
IN SEARCH of a chemical conversation, we are on a farm in Uniow, a little Ukrainian village in Austro-Hungarian Galicia, just before the onset of World War I. In the farm yard we see a big, steaming, lead-lined iron pot. The men have mixed some potash in it (no, not the pure chemical with composition KOH from a chemical supply company, but the real ash from burning good poplar) and quicklime, to a thickness that an egg—plenty of eggs here, judging from the roaming chickens—floats on it.

Elsewhere in the yard, women are straining kitchen grease, suet, pig bones, rancid butter, the poor parts skimmed off the goose fat (the best of which had been set to cool, cracklings and all). This mix doesn't smell good; they would rather toss the kitchen leavings and bones into the great iron pot, but the fat must be free of meat, bones, and solids for the process to work.

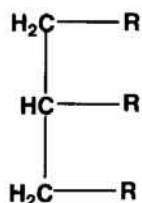
They are making soap. Not that we had to go that far, near where one of us was born, for soap was prepared in this way on farms since medieval times well into this century. Fat was boiled up with lye (what the potash and quicklime made). The reaction was slow—days of heating and stirring until the lye was used up, and a chicken feather would no longer dissolve in the brew. One learned not to get the lye on one's hands. The product of a simple chemical reaction was then left in the sun for a week, stirred until a paste formed. Then it was shaped into blocks and set out on wood to dry.

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And inside the steaming pot, deep inside, where the fat and the lye are reacting? *There* is the conversation we are after, a hellishly animated molecular conversation. The lye that formed was an alkaline mixture of KOH, Ca(OH)₂ and NaOH. In the vat one had hydroxide (OH⁻) ions, and K⁺, Ca²⁺, Na⁺ all surrounded in dynamic array and disarray by water molecules. Contaminants aside, the fat molecules are compounds called esters, in which an organic base, glycerol, combines with three long-chain hydrocarbon chains. A typical chain is stearate:

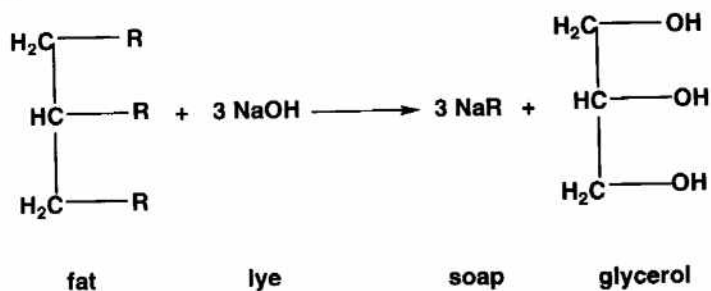


If we call just this ion R⁻, then the formula for a fat is roughly



The reason we say “roughly” is that animal and vegetable fats are not just made of the esters of stearic acid, but also of other long chains containing fourteen to eighteen carbon atoms and associated hydrogens. Hardly anything in this world is simple (only political advertisements and the aesthetic prejudices of people who believe that beautiful equations must be true), least of all the products of evolution, which include fats and the human beings who invented the craft of making soap without waiting for professional chemists to tell them how to do it.

And what is soap? A typical soap is sodium (or potassium) stearate, NaR, where R is the stearate group. The reaction in the pot is:



It's a mad dance floor inside the pot. Some 10^{25} molecules of fat are jiggling around in the viscous solution, moving much quicker (if tortuously) than we may imagine. The molecules collide with each other very frequently, as well as with the OH^- , Na^+ , K^+ , Ca^{2+} ions and waters. Once in a while a hydroxide nears one of the three central carbon atoms of a fat molecule, the knock is just right (men and women are not that different from molecules as they think) and a C—OH bond forms, while the C—R bond loosens. An R^- ion slides into the murk, picks up some surrounding waters, and is off onto the dance floor, picking up a positive ion partner.

One of the authors [RH] has a fond remembrance of the closest model he has seen for molecular collisions and reaction kinetics. It was outside of Havana, an immense crowd densely dancing as the greatest Cuban band of them all, Los Van Van, played "Muevete."

Lye and fat talk, the triglyceride and hydroxide ions sing this wild riff, entangling, reacting . . . in the dark of the deep, except that sunlight comes in, and other energy in the form of heat, more energy to be released when nearby bonds are productively broken. The conversation becomes more heated, old bonds are loosened, new ones formed.¹ Eventually, the conversation quiets, and we have . . . soap.

Is this an excess of anthropomorphism? Molecules, even though they respond to energy and collisions, do not talk. Human beings do. What business do we have, really, to talk of a

molecular conversation? Indulge us for a while, and we shall see. Or hear.

Spin to Spin Talk

Scientists have instruments for eavesdropping on conversations of an ensemble of molecules at the microscopic level. These are totally factual chats, as when we book an airline ticket over the phone and supply the clerk with a credit card number. One particular example is provided by nuclei (or electrons) of atoms informing each other of their spin state.

Hydrogen nuclei, for instance, are allowed by the rules of quantum mechanics two spin states, which are often called "up" and "down," but which, for convenience here, we shall term the blue and the red. Such nuclei can be induced to put up either a blue flag or a red flag (so to say) to signal to us their spin state. The inducement is application of one magnetic field and tickling by another.

Now imagine two such nuclei (call them *A* and *B*) not too far from each other. There are four combinations of spins possible (flags they can wave): (red *A*, red *B*), (blue *A*, red *B*), (red *A*, blue *B*), and (blue *A*, blue *B*). If those nuclei are ignorant of each other's presence, the four sets would have equal energy. But the nuclear spins do feel each other, just a little, and with the help of a strong magnet we can translate that feeling into a difference in energy between those four sets, and eventually into lines in a so-called spectrum. These lines speak to us, they tell us that there are two nuclei there, sensitive to each other. And not three or five, for those would give rise to a different number of peaks and plateaus. Precious knowledge, and we have gotten it by tapping in, nondestructively, on an atomic conversation.

A version of the technique we have just described is used for noninvasive mapping of the inner parts of the body. Once called nuclear magnetic resonance (NMR), it got rechristened in the

