The nature of organic contaminants in nature:

An easy to understand explanation of the physical chemistry behind concerns that leftover crude oil compounds could end up in the critters of Red Butte Canyon

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Big questions about oil spills

Has 70% of the oil in the Gulf really disappeared?

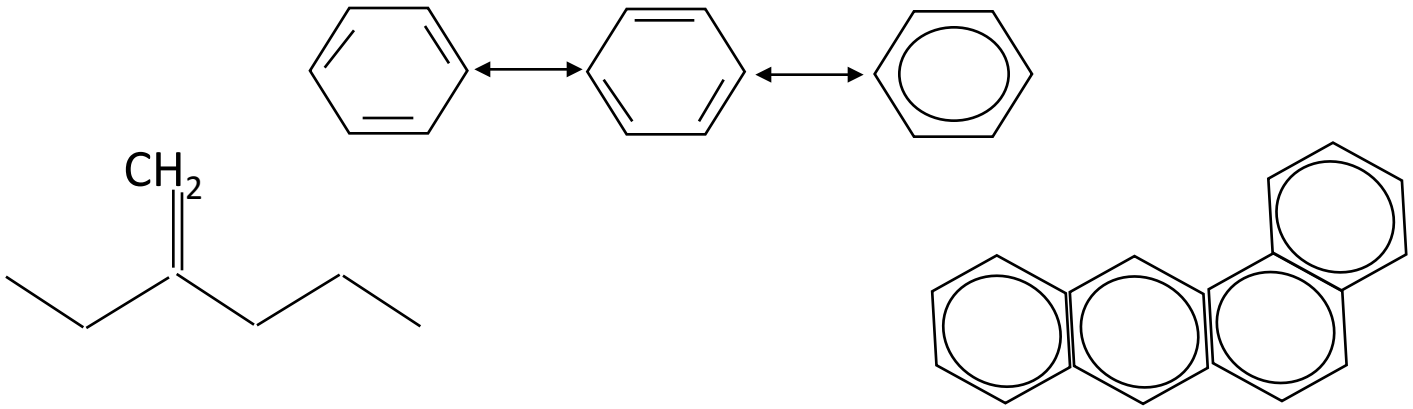
Has the oil really been removed from Red Butte Creek?

How clean is actually clean?

Why are these such difficult questions to answer?

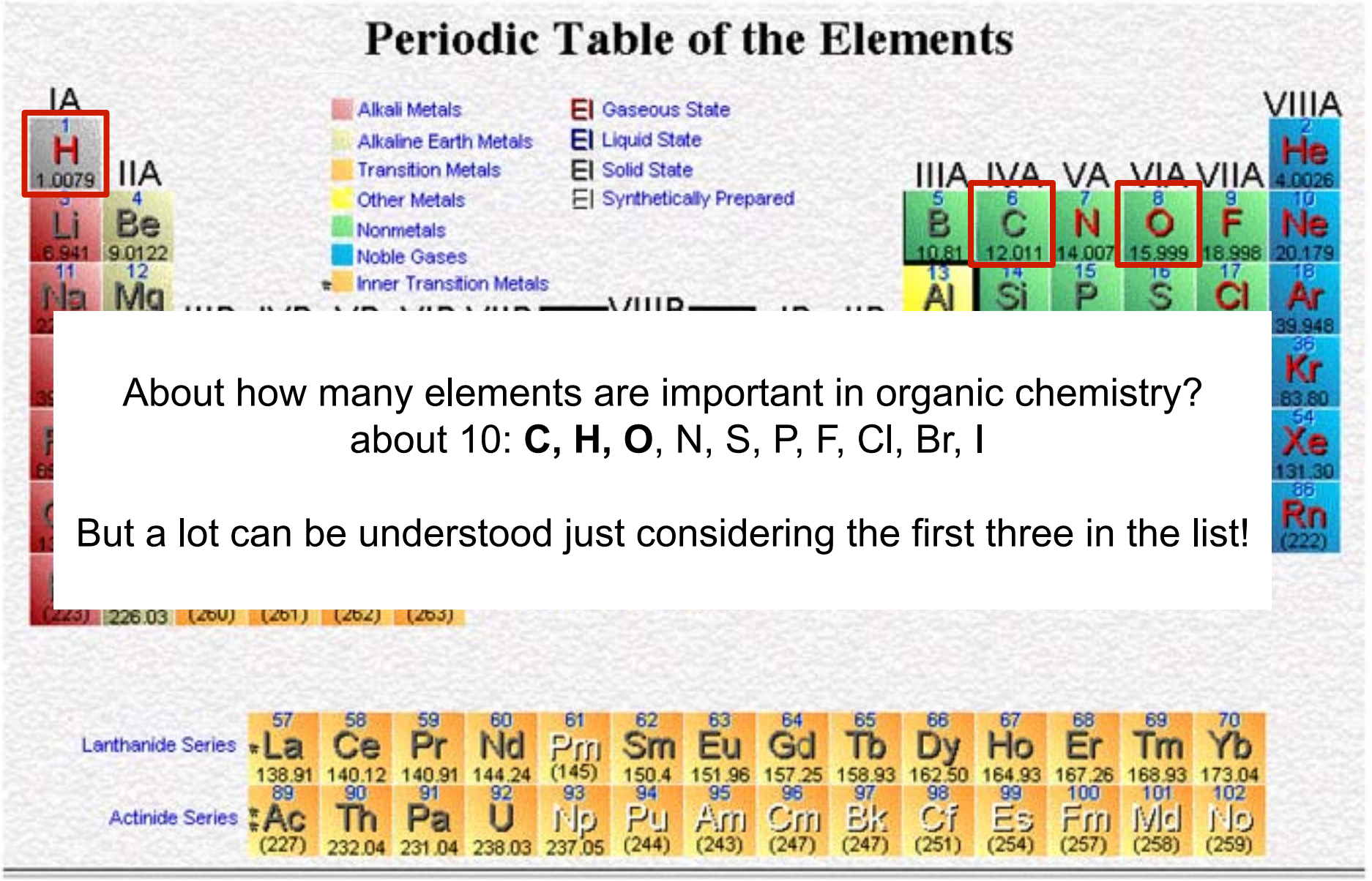
The problem is that crude oil isn't just one compound, but is made up of a wide variety of compounds of differing behaviors

But rather than just TELL you about the differences, I'd like to show you WHY they occur. But to do so first I need you to understand this symbology:

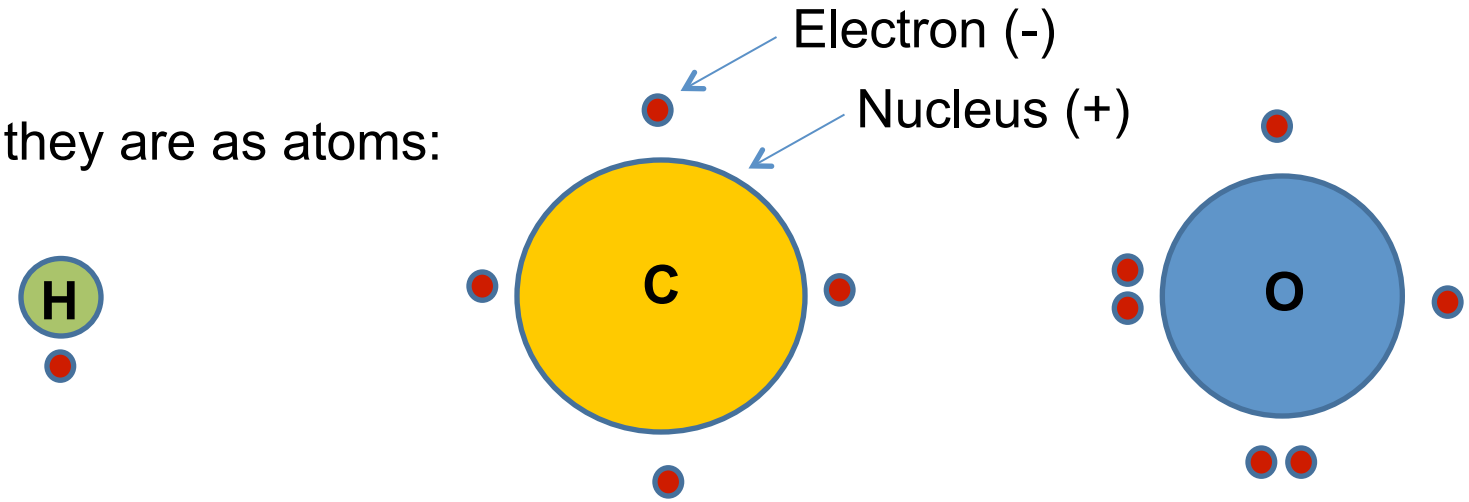


Why? Because they denote structures of organic compounds. No pictures exist of organic compounds – too small – so we use drawings

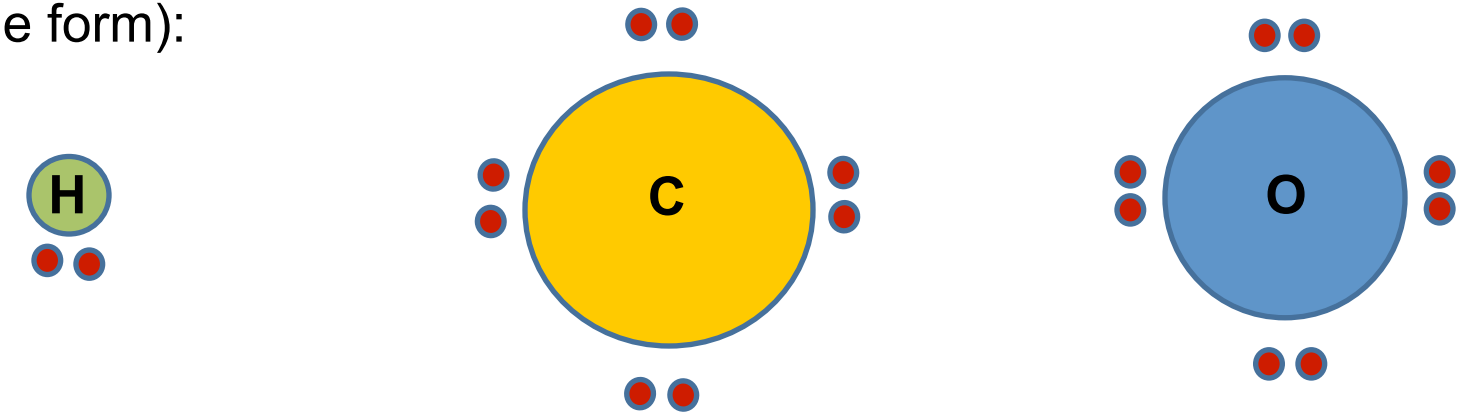
First we need to start with the elements that make up these compounds


Periodic Table of the Elements
Alkali Metals
Alkaline Earth Metals
Transition Metals
Other Metals
Nonmetals
Noble Gases
Inner Transition Metals
Gaseous State
Liquid State
Solid State
Synthetically Prepared
About how many elements are important in organic chemistry?
about 10: **C, H, O**, N, S, P, F, Cl, Br, I
But a lot can be understood just considering the first three in the list!
Lanthanide Series
Actinide Series

What they are as atoms:

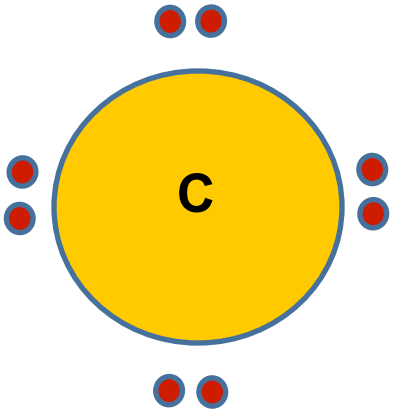


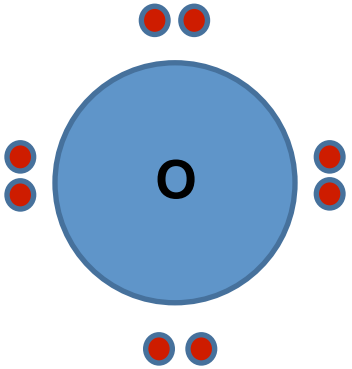
What they want to be (stable form):



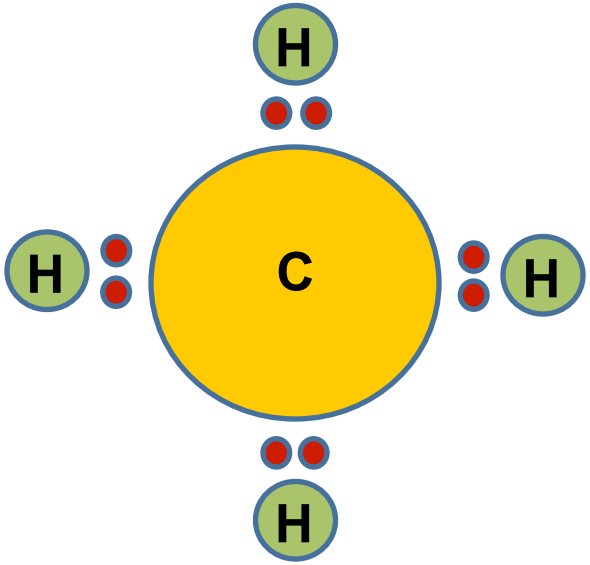
But they can't just steal electrons, so they cooperate (share electrons = covalent bonds)

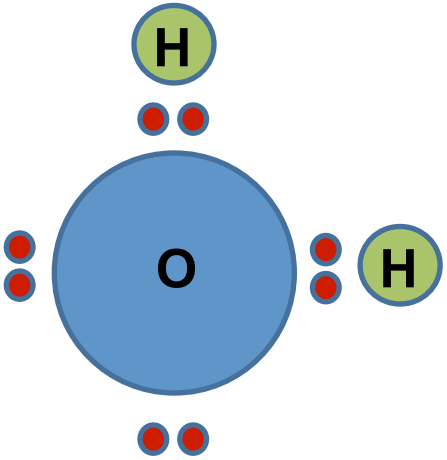
What they want to be (stable form):





Example stable combinations:

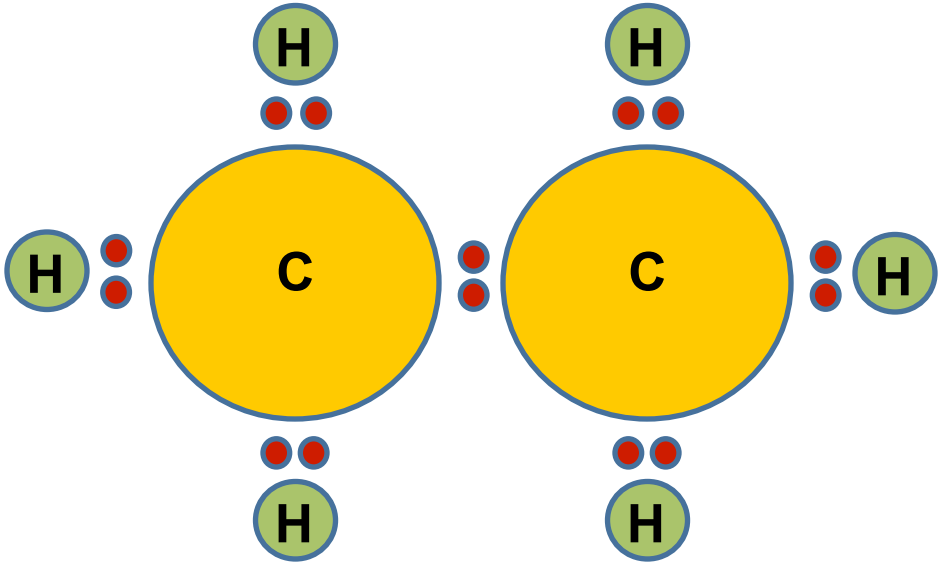




CH_4 = methane

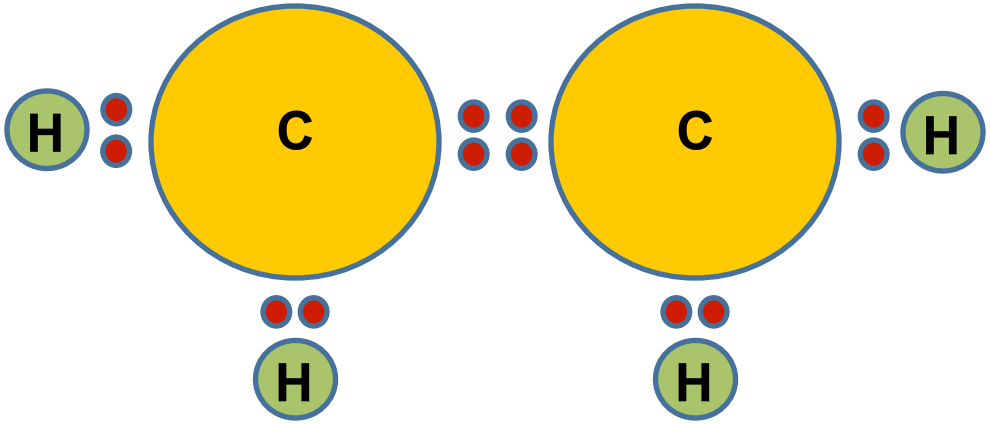
H_2O = water

ethane structure



$CH_3—CH_3$

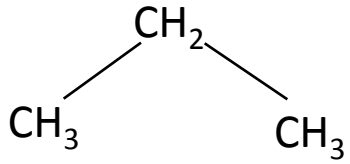
ethene structure

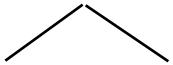


$CH_2=CH_2$

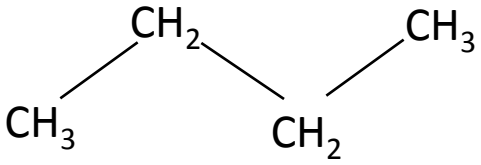
Chains: alkenes and alkanes

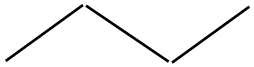
propane



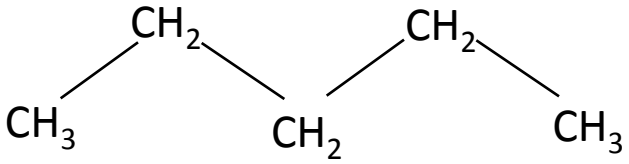


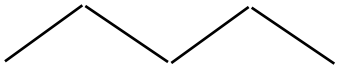
butane



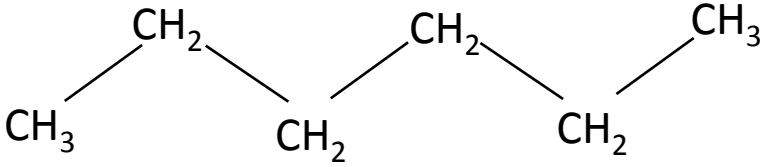


pentane

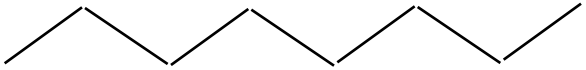




hexane



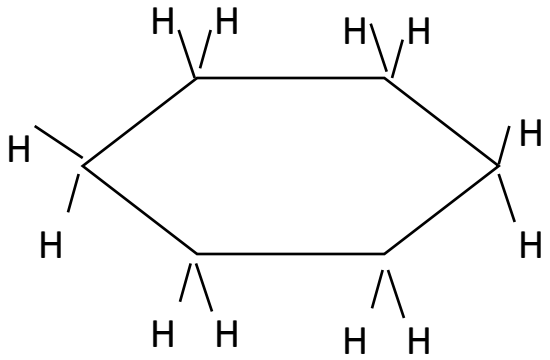
octane



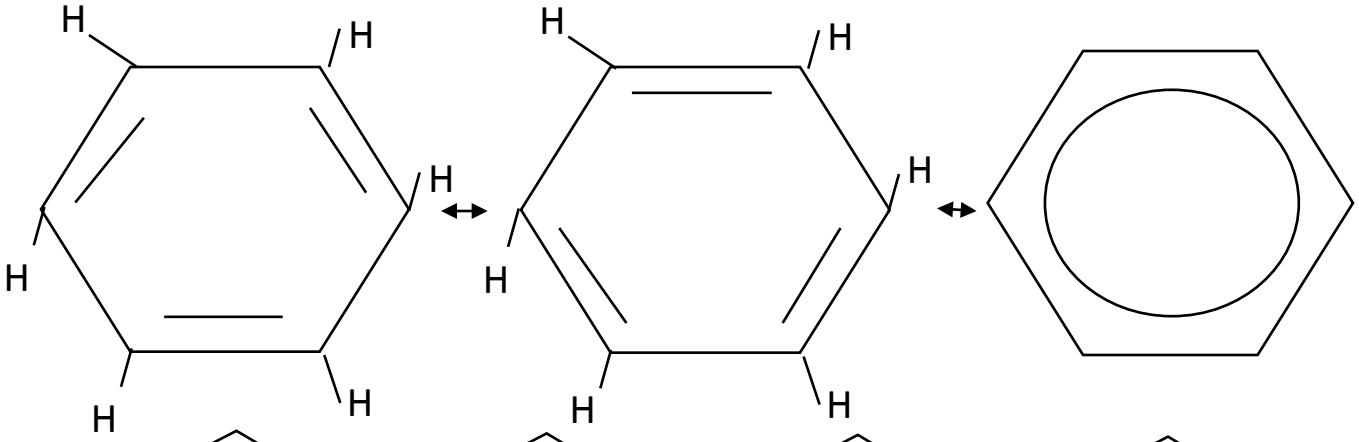
Goes on onto dodecane (12 C) and beyond … “enes” have double bonds

Rings: aliphatic and aromatic

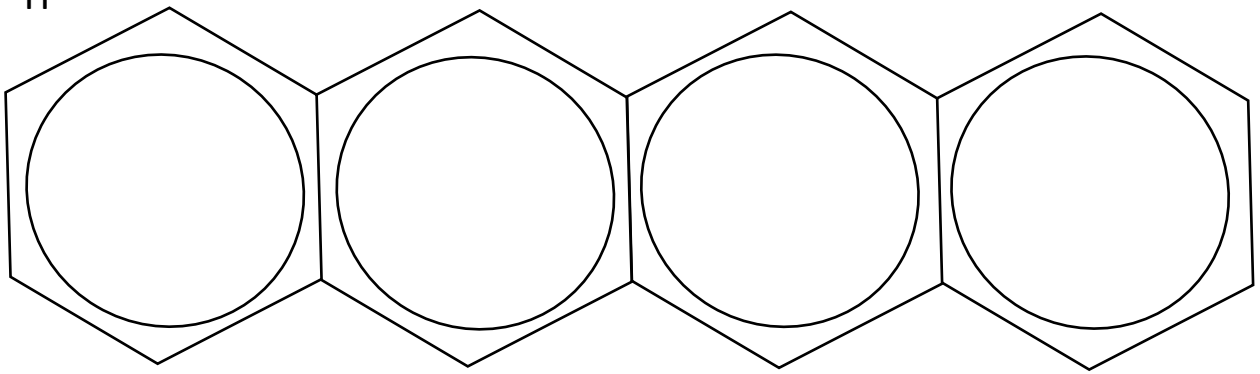
cyclohexane
(aliphatic)



benzene
(aromatic)



fused rings
polyaromatic
hydrocarbons
(PAH)

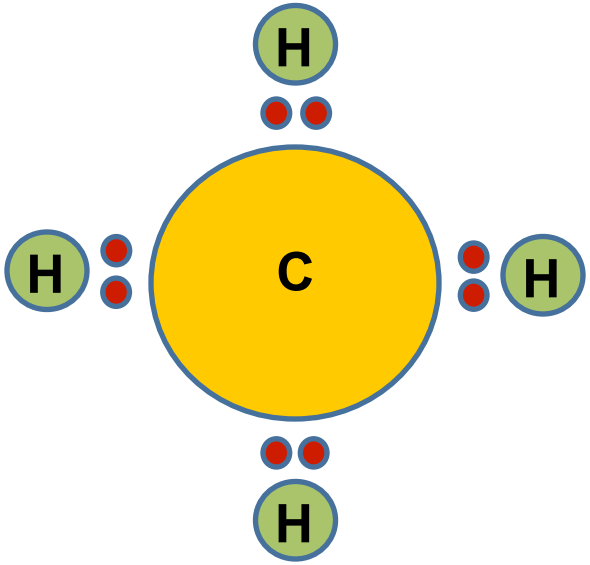


Enough about structure!

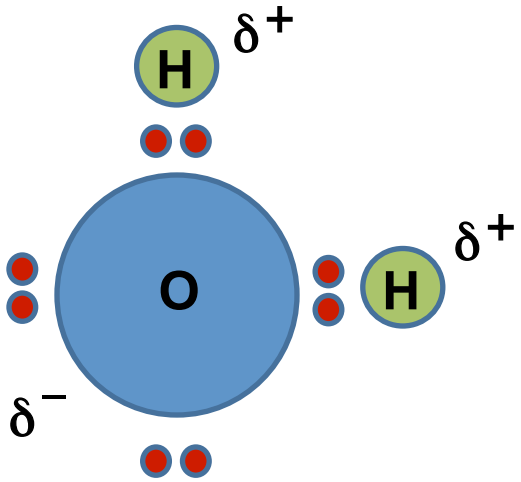
Now that we know about structure we can talk about the "why" of their behaviors

The first thing you need to know is that:

O is an electron hog! and that C and H are NOT electron hogs



CH_4 = methane



H_2O = water

Highly electronegative atoms draw e$^-$ toward themselves. Electronegativities increase with increasing kernel charge, and decreasing kernel size. Thus electronegativity increases across rows, but decreases down columns, of the periodic table.

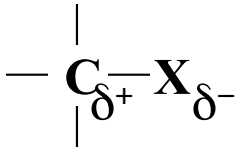
TABLE 2.3 Electronegativities of Atoms According to the Scale Devised by Pauling (1960)

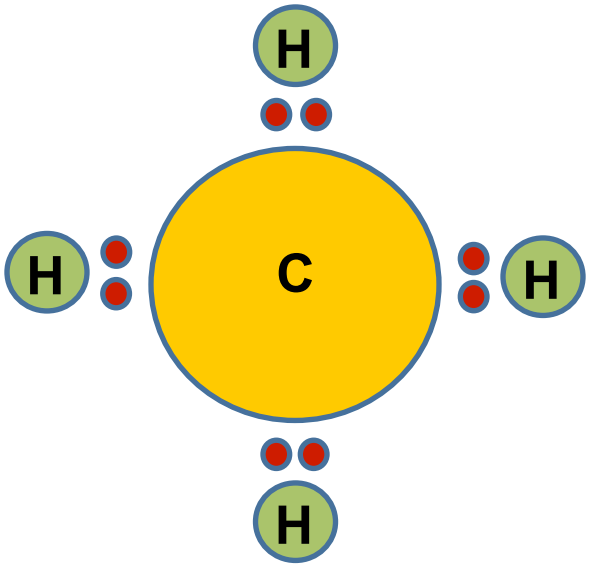
Charge of kernel:	+1	+4	+5	+6	+7	
	H					Increasing size of kernel ↓
	2.2					
		C	N	O	F	
		2.5	3.0	3.5	4.0	
			P	S	Cl	
			2.2	2.5	3.0	
					Br	
					2.8	
					I	
					2.5	

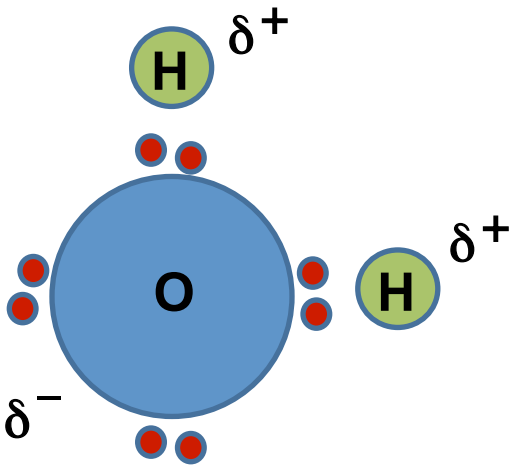
Source: Schwarzenbach et al, 1993

Second row atoms (e.g. N, O, F) are more electronegative than the atoms in the same column but in lower rows in the periodic table.

In a diatomic bond, the e$^-$ cloud is directed toward the atom with the higher electronegativity.







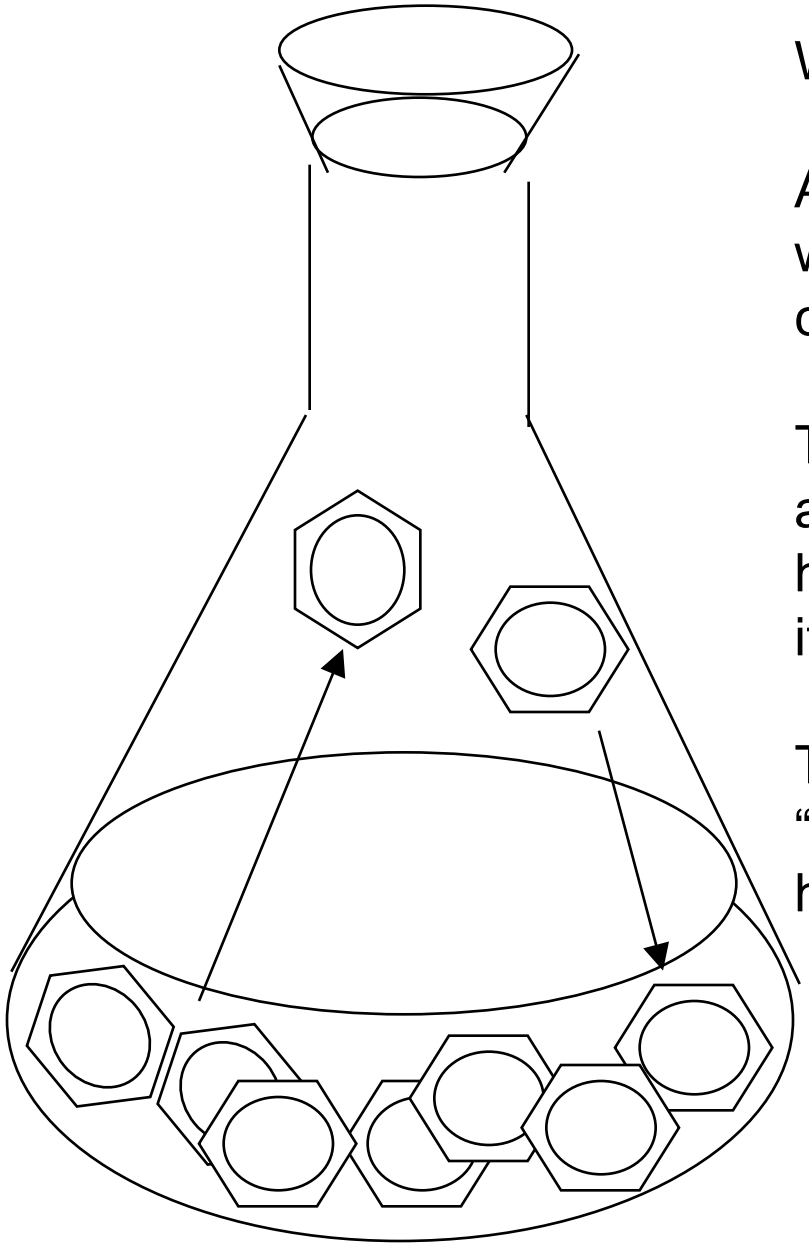
C-H bonds are "**non-polar**" since the electrons are evenly shared across the bonds

O-H bonds are called "**polar**" since there is a positive pole (H) and negative pole (O) across the bond

Same is true for C-O bonds

Polar versus non-polar bonds dictate organic compound behavior

First: vaporization (moving the molecule from its own liquid to air)



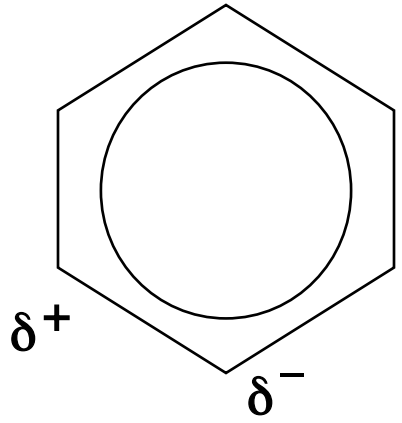
What's involved in vaporization?

A molecule "breaking" interactions with its neighbors in the liquid (e.g. crude oil)

The pressure of the compound in the air space of a stoppered container holding the liquid compound is called its vapor pressure

The easier it is for the compound to "break away" from it's neighbors, the higher its vapor pressure

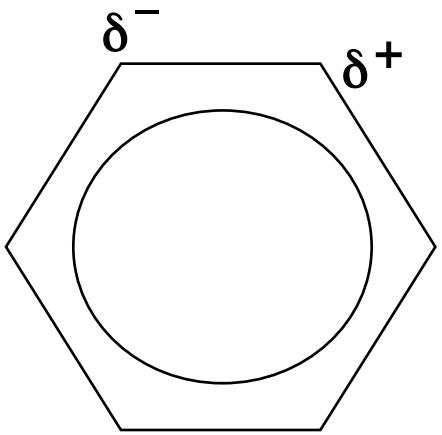
What interactions are involved?



So called “van der Waals” forces that occur between all molecules.

They result from instantaneous skewing of the electrons in any bond between atoms.

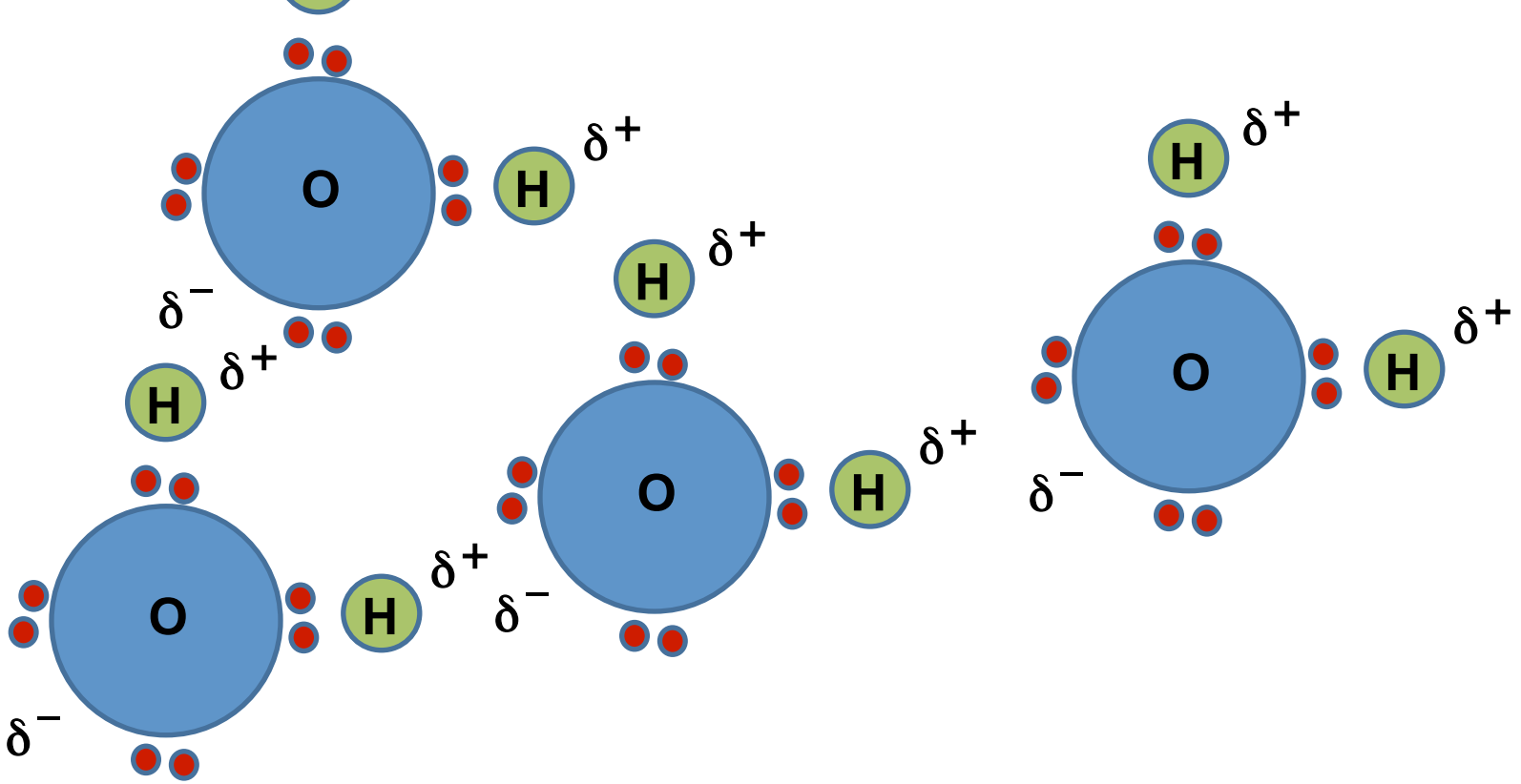
This skewing forms a fleeting dipole in the bond.



When the fleeting dipole occurs, it triggers a complementary dipole in neighboring molecules.

Since opposites attract, the molecules attract one another for a fleeting moment.

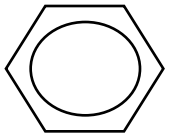
This happens continuously (but fleetingly) for all bonds in a molecule. The resulting attractions work to hold molecules close together in the liquid.

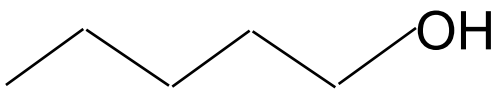


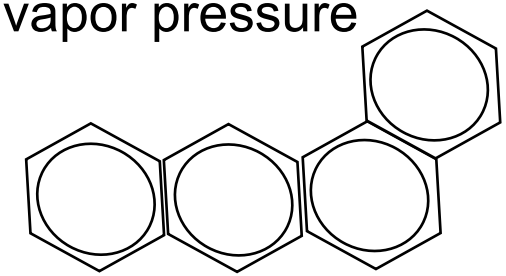
In addition to fleeting van der Waals interactions, molecules may have permanent polar interactions, e.g. water, or organic compounds with C-O bonds.

These polar interactions add to the interactions holding molecules together in the liquid. In order to break free of the liquid, a water molecule must break free of these polar interactions as well as the van der Waals interactions holding it close to its neighbors

Put these compounds in order of increasing vapor pressure







Vapor pressure increasing

Which ones would disappear first from a spill on the ground surface?

Another behavior to consider: dissolution into water

Mmm … you taste like crude oil

Dissolution into water: the short story:

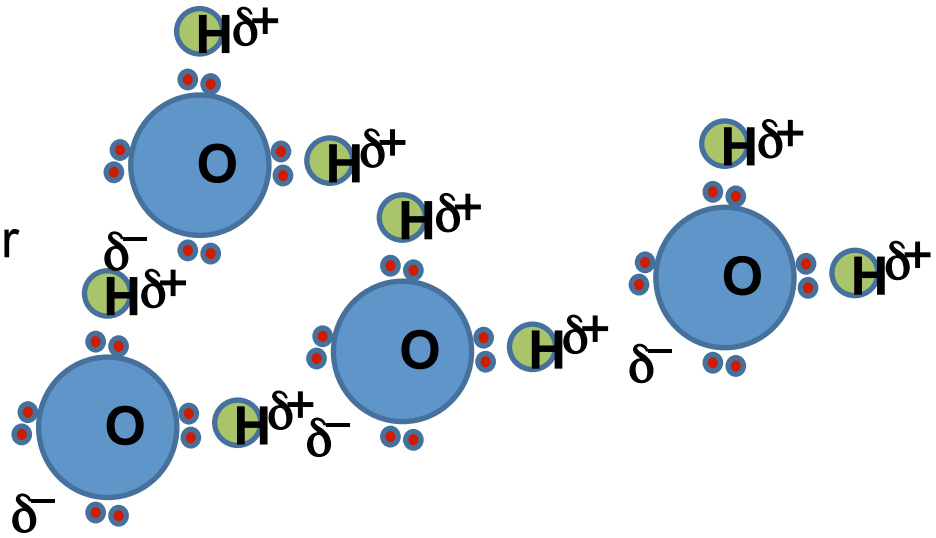
"Like dissolves like"

Polar dissolves polar

Non-polar dissolves non-polar

Oil and water don't mix

Why?

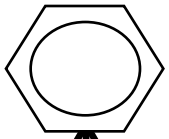


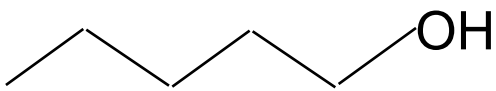
Water is polar and has a structure that results from those polar interactions

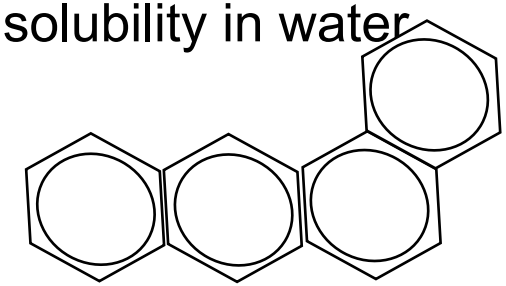
Non-polar organic compounds are not well-accommodated by water

They call non-polar organic compounds "hydrophobic" = "water fearing"

Put these compounds in order of increasing solubility in water







Solubility in water increasing

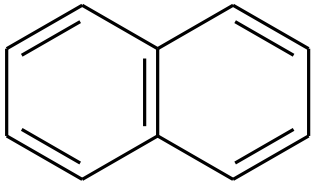
Which ones would disappear first from a spill in water?

Biodegradability also roughly follows this trend (smaller = more degradable).

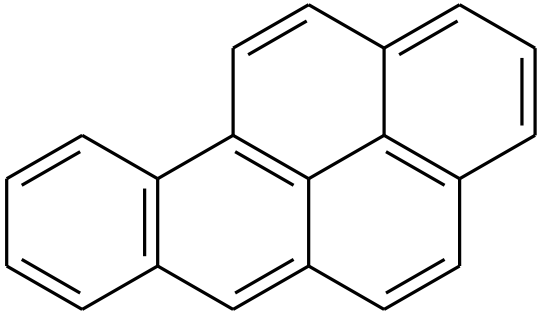
O.K. which ones would remain in a spill exposed to air and water?

Polycyclic aromatic hydrocarbons (PAHs)

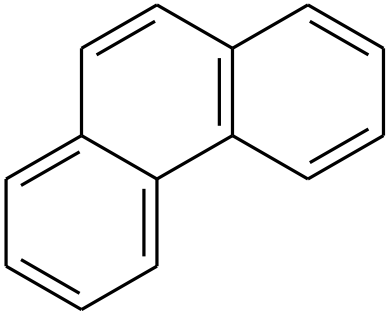
The stuff that sticks around
(doesn't vaporize or readily dissolve or degrade)



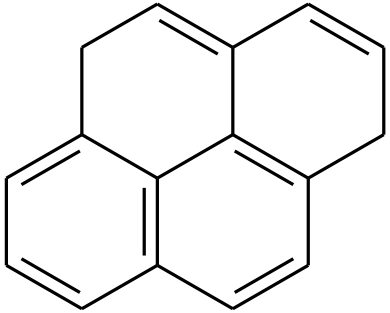
Naphthalene



Benzo(a)pyrene



Phenanthrene



Pyrene

Long history of PAH toxicity

1775: Sir Percival Pott reported high rates of cancer in London chimney sweeps. Attributed to a carcinogenic component in fireplace soot

1880's: High rates of skin cancer reported for workers in paraffin refinery, shale oil, and coal tar industries

1915-8: Japanese scientists showed that repeated painting ears of rabbits with coal tar induced tumors

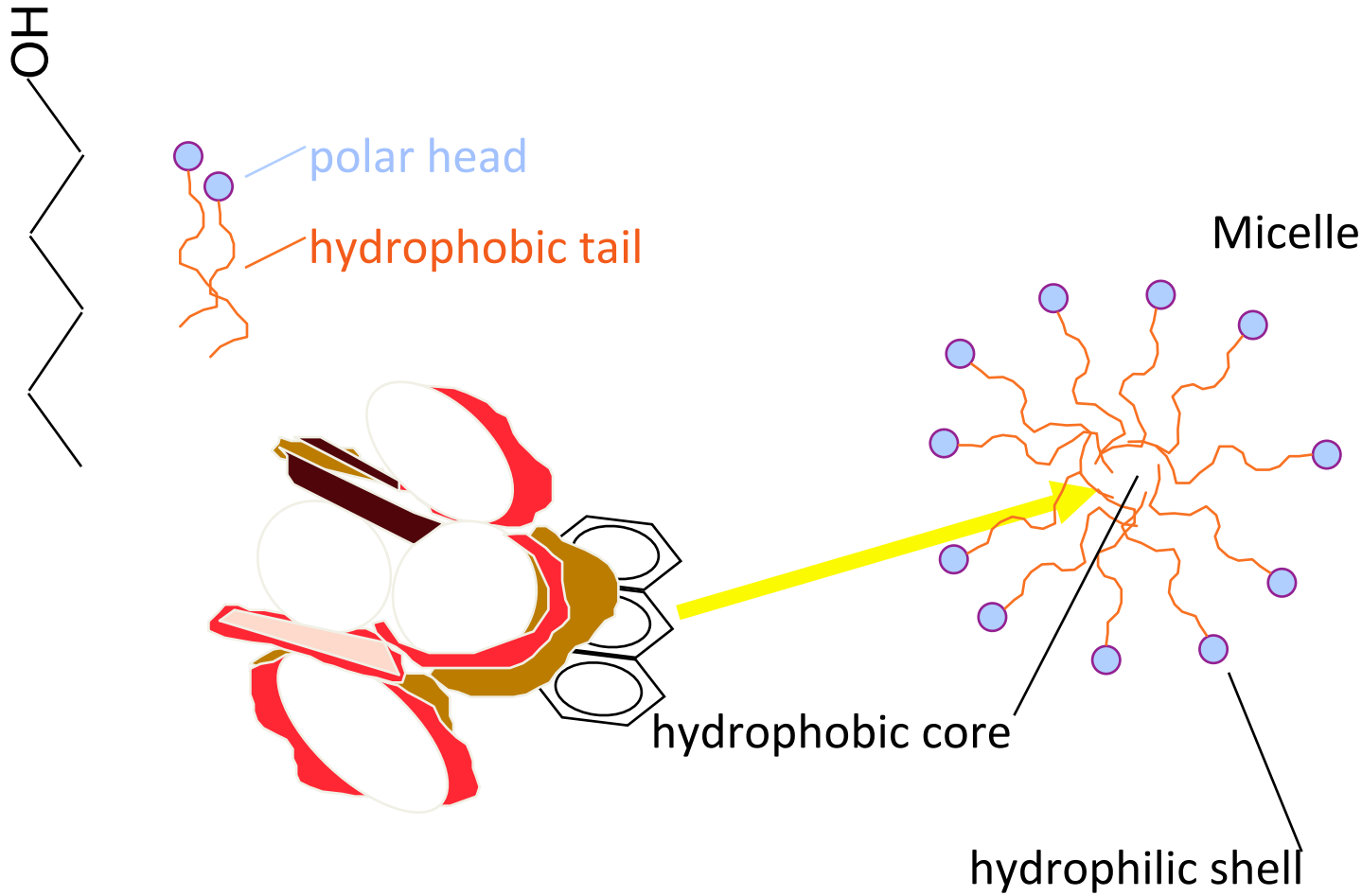
1922: Organic extracts of soot are carcinogenic

1933: Kennaway *et al.* – isolation of the "coal tar carcinogen", Benzo(a)pyrene; first example of a pure chemical compound demonstrating carcinogenic activity

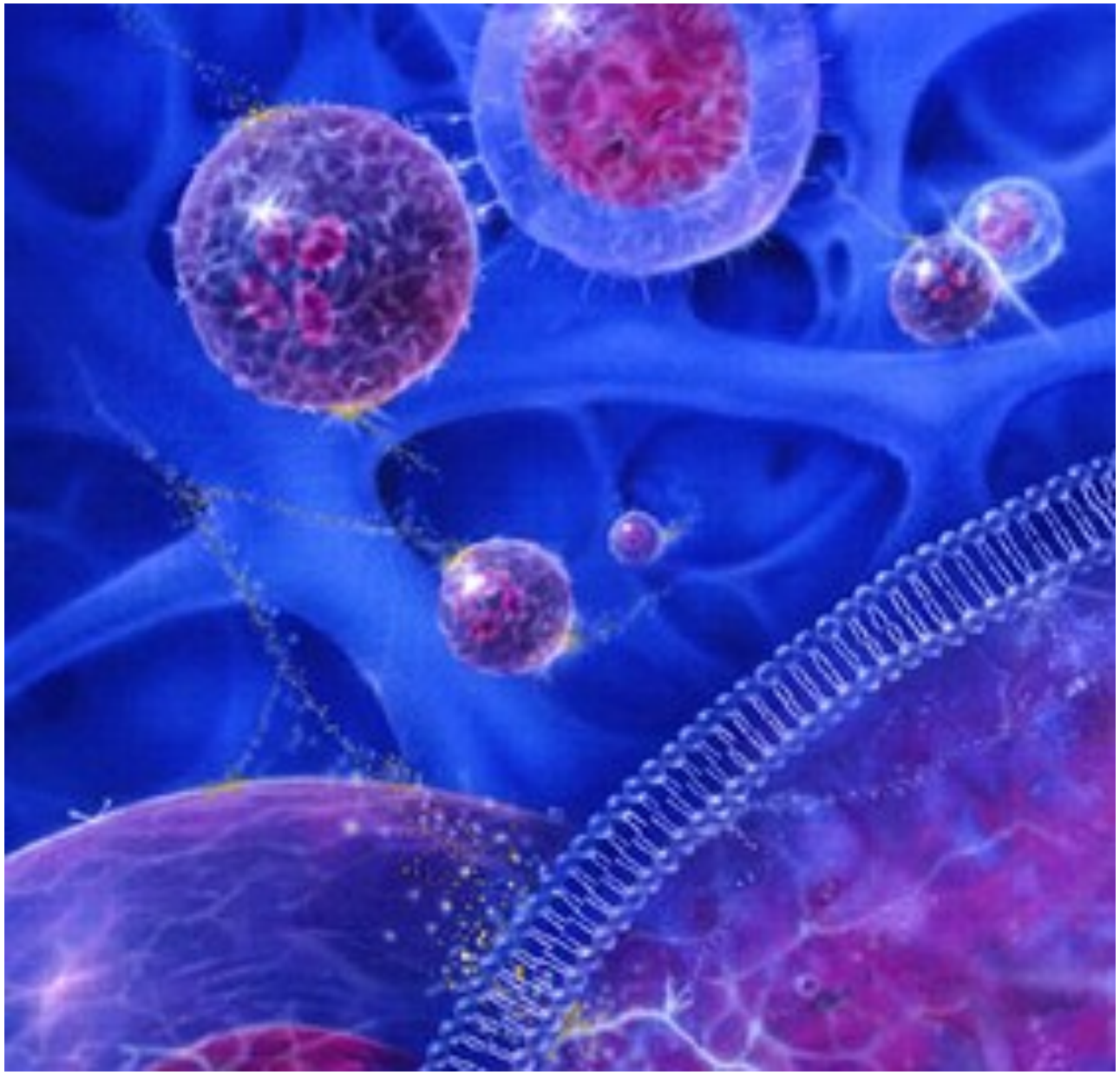
1942: Extracts of ambient particulate matter are carcinogenic

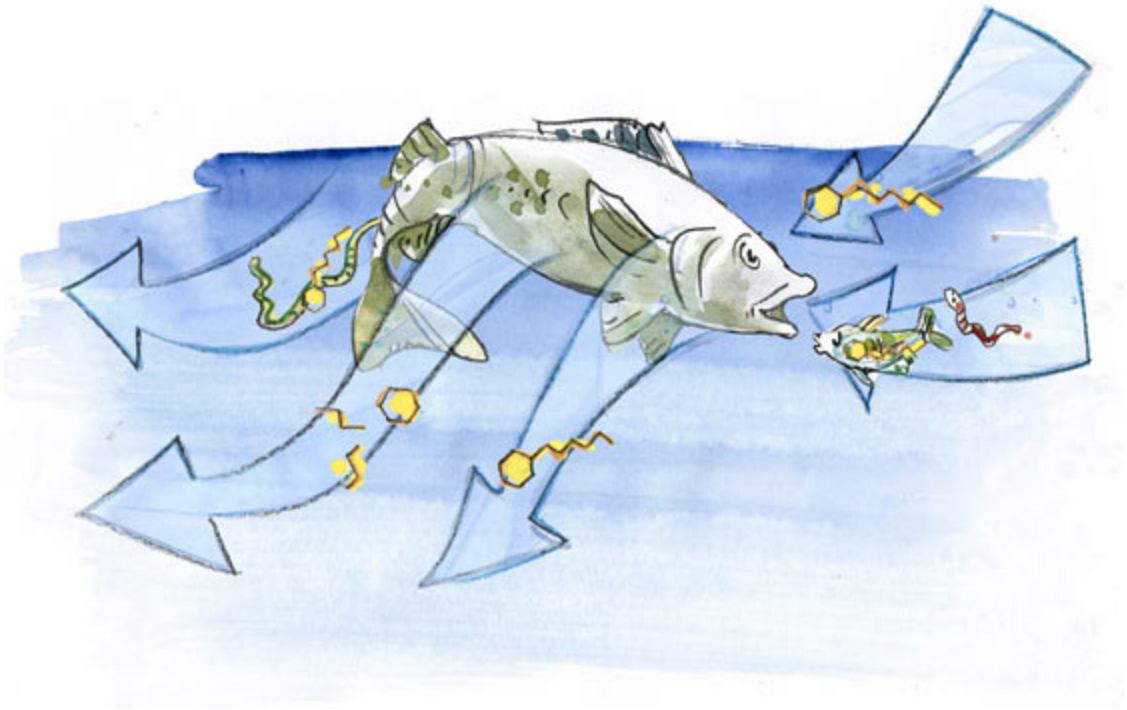
Why do they end up in biota?

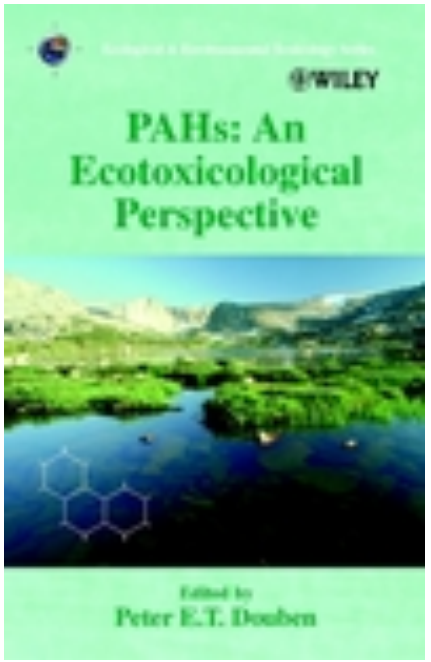
Biological cell membranes are basically little sponges, made of the same stuff they use for oil spill dispersants (to coax oil compounds into, and mix with, water)



Cell membranes are basically two-layer micelles



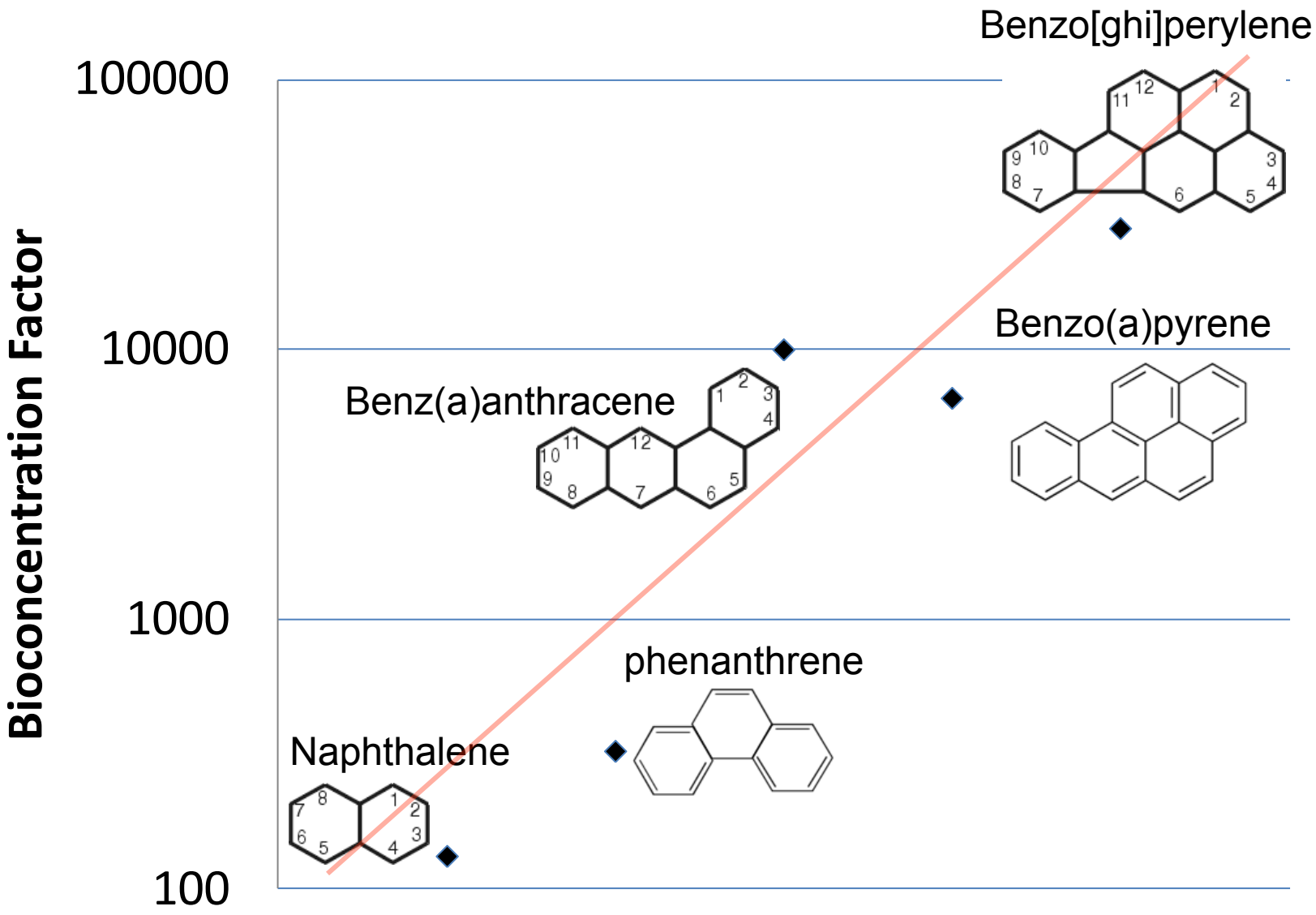




PAH bioconcentration occurs in cells

bioconcentration factor = conc in critter/conc in water

values can be quite high


Benzo[ghi]perylene
100000
10000
1000
100
Bioconcentration Factor
Benzo(a)pyrene
Benz(a)anthracene
phenanthrene
Naphthalene

So as bad as the vaporized compounds smelled and the dissolved compounds looked; what remains?

What will be the ultimate impacts? Relative to other impacts?