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13 heaviest gases

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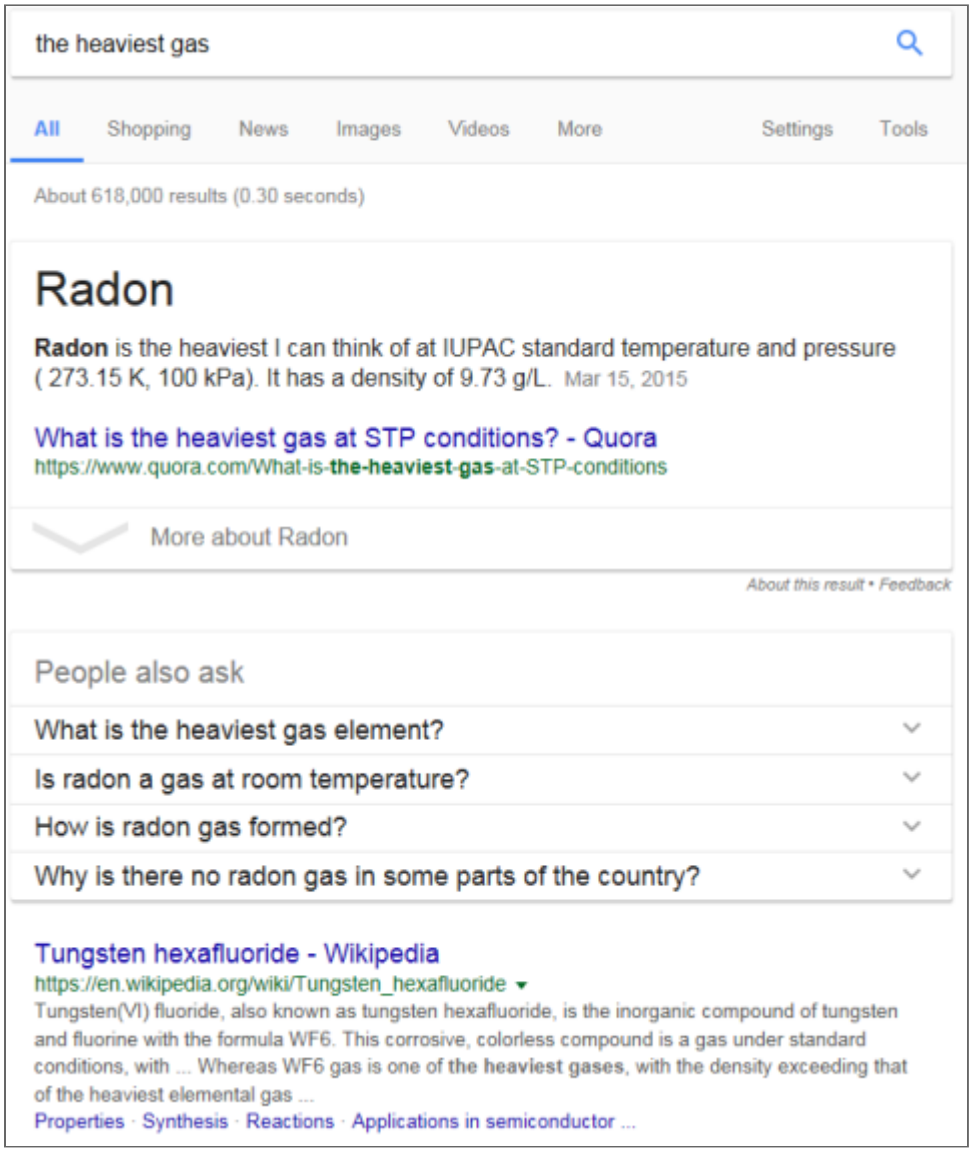
Nothing predicted a destination of a seemingly benign Internet search. I just Googled "the heaviest gas". I chuckled at the output:



For sure, the first result (Radon) was wrong by a great margin. The second (WF_6) was much closer to truth, but I decided to spend 10 minutes to check if Mother Nature knows anything heavier than that.

Ten months later I said to myself: "you've got to stop!"

I had to repeat that several times. Remind myself that refreshing dynamic programming or methods of clustering is much better for my career rather than chasing obscure gases. Recall that I'm not even a chemist.

That quest was... addictive. Unexpectedly addictive.

Did I say "obscure"? Sure enough, the further my search went, the stranger and stranger compounds I met, some clearly known only to a handful of people on Earth. $Mo_2((CH_3)_2N)_6$, anyone? Some were apparently so little known that I started seeing typos or errors in numerous "*Dictionaries of This and That Compounds*" that I dealt with. Clearly, I reached some very dusty fringes of the Forest of Gases. Yet every new chemical offered new ideas and challenged: "hey can you find anything heavier than me that is still a gas?"

I stopped when my tracking Excel hit 340 records.

But then I felt sad thinking that all these results "will be lost in time". So I decided to share some with you. Therefore, here is the list of some of the heaviest gases that exist in Nature. Plus a bit of bonus material.

Disclaimer. For the purposes of this article, a "gas" is any substance with a boiling temperature less than +20 C at normal atmospheric pressure, and stable enough at those conditions to measure that. "Heavier" simply means molecular weight. While that is not completely precise, I seriously doubt that anybody has ever made enough of some of these chemicals to determine their exact density in the gaseous form.

Part 1. Beyond Radon.

1. We will start with **$SF_5C(O)CF_3$**. With a molecular weight of 224 and a boiling point of 15.6 C [10], this is probably the heaviest gas containing Sulfur -- 1.5x times heavier than a well-known SF_6 and 7.8x times heavier than air. Some people breathe SF_6 to speak in low-toned voices. For sure, I would not recommend trying that with $SF_5C(O)CF_3$, provided that you get enough of it somewhere, somehow.

2. Let's continue with **$N(CF_3)_2CF=CF_2$ (**m.w. 233, b.p. 13.7 C, [20, page 648]). It is a fire suppressant candidate. There is a whole industry dealing in these kinds o compounds. For application in aviation, they must have boiling points of less than -40 C, and often have to contain Fluorine, Chlorine or Bromine, thus being rather heavy. Acceptance to this club is strongly restricted to only those chemicals that show no adverse health effects in humans.

3. $P(CF_3)_3$ [m.w. 238, b.p. 17.3 C, (30, page 323]), AKA tris(trifluoromethyl)phosphine, is probably the heaviest gaseous phosphorus compound.

4 & **5**. **C_4F_{10}** and another **C_4F_{10}**. Their molecular weights are the same 238, yet structurally they are different. One is Perfluorobutane, another Perfluoroisobutane, with the boiling temperatures of -1.7 C [50] and 0 C [60, page 6-70]. The first one is used for "microbubble ultrasound contrast agents", so *maybe* is not very toxic. Theoretically, the speed of sound in that gas is only 11 m/s under normal conditions, that's enough to turn 5th octave C into 3rd octave F#, provided that it won't cause an unconsciousness via the anesthetic effect, of which I'm not sure.

6. The next one is better be met only in a well equipped lab: Tellurium Hexafluoride **TeF_6** (m.w. 241.6, b.p. -37.6 C [70]). It is "a colorless, highly toxic

gas with an extremely unpleasant smell." I always wondered -- how do people know that? Were there any brave souls who actually smelled it?

7. Pentafluoroiodoethane **CF_3CF_2I** (m.w. 245.9, b.p. 13 C, [80, page 424], [90]). Start with a good old ethane C_2H_6, replace one Hydrogen with Iodine and the res with Fluorine. Listed as a potential anesthetic in [80], it *probably* is not poisonous - if knocking oneself out or overdosing does not count.

8. Same applies to decafluorodiethyl ether **$C_4F_{10}O$** (m.w. 254, b.p. 0 C [80, page 413]).

9. The next compound, perfluoropropyltrifluoromethyl ether **$CF_3OCF_2CF_2CF_3$** (m.w. 254, b.p. 6.74 C, [20, page 650]) although seemingly belonging to the sam family is listed as a potential fire suppressant.

10. **F_5TeOF** (m.w. 257.6, extrapolated b.p. 0.6 C, [100, page 778]). Presumably named "Tellurium hypofluorite", presumably toxic and malodorant.

11. Pretty much anything volatile with Tellurium in it is at least modestly harmful and does not smell welcoming. That applies to the next gas **$TeClF_5$** Tellurium (VI) chloride fluoride (m.w. 258, b.p. 13.5 C, [100, page 776]).

12. Iodine heptafluoride **IF_7** (m.w. 259.9, b.p. 4.8 C, [110]) -- a whole nine times heavier-than-air gas. Chemically reactive, dangerous. "Can cause fire on contact with organic material." Looking at its formula, one might get an idea: why don't w substitute one Fluorine with something heavier, say Chlorine, and arrive to an even heavier $ICIF_6$? After all, that worked with $TeClF_5$. Unfortunately, according t Wikipedia, there are virtually no interhalogen compounds featuring more than tw halogens. So this is a dead end.

13. **WF_6**, a famous Tungsten Hexafluoride (m.w. 297.83, b.p. 17.1 C, [120]). Wikipedia cautiously names it "one of the heaviest gases", but provides no examples of anything heavier. We will see why as we move forward. For now, it suffices to say that WF_6 is a well-studied chemical, used in semiconductor industry to deposit thin layers of Tungsten on Silicon. However, purchasing this gas for a home collection isn't a good idea. Corrosive, poisonous and chemically active, it is better admired on the picture rather than in an ampule.

At this moment, we are entering the realm of the **Doubtland**.

Part 2. The Doubtland.

The first habitant is **$Ge(CF_3)_3F$**, tris(trifluoromethyl)fluorogermane. With a molecular weight of 298.65, it is just 0.28% heavier than WF_6. It definitely exists, as multiple sources suggest (e.g., [130, page 61] or [140]). They both provide 19.1 C for its boiling point, so technically it is a gas.

Any issue with that?

Well, if you read the paper [140], you'll encounter the note that says: "*The fluorid is also anomalous in that all of the other newly prepared compounds appear to b monomeric liquids or solids except $(CF_3)_3GeF$. As shown in Table 11, the sublimation point of this compound is normal in comparison with the other halide but the melting point, 30 °C, is quite abnormal, about 125 °C above the melting point of $(CF_3)_3GeCl$. This shows extensive association in the solid state, probabl by means of fluorine bridging between germanium atoms.*" And the article's boilin point of 19.1 C is "extrapolated", with the melting point given of 27-30 C. I am not exactly sure how to interpret that. Is that a solid, contrary to a very volatile molecular $Ge(CF_3)_3Cl$ (b.p. 37 C) and $Ge(CF_3)_3Br$ (b.p. 49 C) ([130], [140])? Har

obtained in 1975. It really feels strange to think if the molecule of $Ge(CF_3)_3F$ was called into existence on Earth only once, by someone's experiment 41 years ago...

Confusion is further enhanced by data sources like chemsrc.com quoting a b.p. o +16 C for an even heavier compound $Ge(CF_3)_3Cl$. But after cross-checking with other sources, I arrived to the conclusion that this is some kind of an error. Chmsrc.com seems to list underestimated boiling points for many compounds (like 6.1 C for a monstrous $Mo_2((CH_3)_2N)_6$).

The Land of Doubt continues with **CF_3-Te-Te-CF_3**. According to [130] and [150, page 22], it has a boiling point of -53 C, while being 1.32x heavier than WF_6! Unfortunately, after extra research I became almost convinced that this is a typo. Many similarly structured but lighter compounds have much higher boiling points such as $Te(CF_3)_2$ (m.w. 265.6, b.p. 23 C, [160]), CF_3-Se-Te-CF_3 (m.w. 344.5, "Orange oil. Mp. < 80. Dec. at 20" per [150]). In comparison, it would be extreme strange for a heavier CF_3-Te-Te-CF_3 to be so more volatile than its lighter "close relatives".

Numerous wonderful errors exist across the literature (try searching $(CF_3)SbI_2$ fo example), but at this point you may be wondering -- are there any citizens of the Doubtland that are not typos? Sure, there are. As much as the Doubtland can be confident, of course.

Welcome **PoF_6**. According to [170], its predicted boiling point is around -40 C. With a molecular weight of 322.97, that for sure would make it quite a strong candidate for the heaviest gas. The "tiny, insignificant problem"? Nobody has managed to synthesize that chemical yet. So we don't really know whether PoF_6 exists in reality.

And the question of "the heaviest gas" remains open, with the answer lost in fractal obscurity of exotic compounds known to only few experts...

Yet the story would be incomplete without a tour of the Almost Made It City, populated by numerous peculiar and curious compounds that were close to being heavier than Radon gases, but did not quite make it.

Part 3. Interesting Almost-Made-It Cases.

Methylated metalorganics like **$W(CH_3)_6$**, **$Pb(CH_3)_4$** (b.p. 100-110 C), or **$Sb(CH_3)_3$** are often volatile. Of those with a m.w. over 222, the most volatile is probably dimethylmercury **$Hg(CH_3)_2$**. Described in [180] as "one of the strongest known neurotoxins", this liquid with a b.p. of 93-94 C is certainly something to keep as fa away from oneself as possible.

Replacing Hydrogen with Fluorine in a CH_3 group offers perfluoromethylated compounds like Bis(trifluoromethyl)selenium **$Se(CF_3)_2$** (m.w. 217, b.p. -2 C, [190, page 427]), **$N(CF_3)_3$** (yes, another a gas with b.p. of -6 C and m.w. of 221, [80, page 425]), or **$Te(CF_3)_2$** (m.w. 265.6, b.p. 23 C [200]). Most are volatile, and mos are heavy -- take a look at the liquid **$Pb(CF_3)_4$** (m.w. 483, [40]) for example. Further substitutions produce an almost endless variety that was too vast to fully explore, like **$As(CF_3)_2Cl_3$** (m.w. 316, b.p. 94 C [30, page 325]), or **$As(CF_3)_2H$** (m.w. 213.9, b.p. 19 C [30, page 325]). I spent a great fortune of time looking at them. Sometimes it felt that the winner -- a gas heavier than WF_6 -- was nearby. Yet in the end, the closest to breaking a records came **$Ge(CF_3)_4$** with a m.w. of 348.6 and b.p. of 31.7 C ([130], [140]). Still not a gas. Still I suspect that a better candidate might be hiding somewhere amongst colorful varieties of trifluorometh substitutes. But I had to stop and attend my own life.

PF_3 can play a role similar to CF_3, giving birth to volatile metal complexes. I foun around forty of them. Some of the marvels are Nitrosyl(phosphorus trifluoride)cobalt **$Co(PF_3)_3(NO)$** (m.w. 352.9, b.p. 81 C [220, page 3049], **$Pt(PF_3)$** (m.w. 547, b.p. 90 C [230, page 1592]), or continuous family **$Mo(PF_3)_{6-n}(CO)_n$**. C all them, the closest to being a gas is probably **$Ni(PF_3)_4$** (m.w. 410.7, b.p. 70.5 C [230, page 1592]).

What else is worth mentioning?

Nickel appears to make the most low-boiling metal carbonyl -- **$Ni(CO)_4$** with a m.w. 170, b.p. 43 C [240]. While other metal carbonyls are often volatile, too (like **$ReH(CO)_5$** or **$Os(CO)_5$**) all of them appear to be solids or liquids.

$U(BH_4)_3(BH_3CH_3)$ is volatile but solid (m.w. 311.2) per [250, page 554]. Other (even simpler) actinide borohydrides are less volatile.

WF_5Cl definitely exists but is "a yellow solid" [260, page 276], **WF_4Cl_2** is "thermally unstable at room temperature, decomposing to tungsten hexachloride and tungsten hexafluoride" [270], and **$ReClF_5$** is "volatile red liq.", "Dec. at r.t. an slowly at -30. Mp -2" (I love that language!) I found it in the same Dictionary of Inorganic Compounds edited by Jane E. Macintyre, but cannot provide you with the link because of the paywalls. Google simply does not return that page anymore, even if I search those exact terms, probably because I have already seen too much of that book without buying it.

That's it. Thank you, and have a nice day!

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