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Education

OXIDATION OF HF WITH $KMnO_4$ AND POSSIBLE MISCONCEPTIONS ABOUT HF[*]

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Is hydrogen fluoride or its aqueous solution really incompatible with $KMnO_4$? If so, in what respect (meaning why)? This contribution seeks to answer the previous question that was posed some 20 years ago on the pages of the Journal of Chemical Education. The previous conclusion was that $KMnO_4$ cannot oxidize fluoride anions to elemental fluorine. However, this does not prevent the possibility of another type of reaction occurring between HF and $KMnO_4$.

In brief, the reaction of HF(aq) and $KMnO_4$(s) cannot occur with concentrated HF(aq), where $w(\mathrm{HF}) \approx 0.4$. However, the reaction of liquefied hydrogen fluoride, HF(l) and $KMnO_4$(s) appears to produce Mn_2O_7(l), which is explosive even at moderate temperatures. The same applies to aqueous solutions of HF where $w(\mathrm{HF}) \geq 0.6$. In this contribution, some details are further explained and the spreading of some misconceptions is, hopefully, hampered.

In addition, some authors described HF as a "flammable and explosive" substance, which is even worse than claiming that "water is flammable and explosive".

Key words: fluorine; hydrogen fluoride; potassium permanganate; manganese(VII) oxide;
flammability of HF

ОКСИДАЦИЈА НА HF СО $KMnO_4$: МОЖНИ МИСКОНЦЕПЦИИ ОКОЛУ HF

Дали флуороводородот или неговиот воден раствор е навистина некомпатибилен со $KMnO_4$? Доколку ова е точно, во која смисла на зборот? Целта на денешниов прилог е да се даде одговор на претходното прашање коешто беше за првпат поставено пред дваесетина години на страниците на Journal of Chemical Education. Краткото образложение беше дека $KMnO_4$ не е во состојба да ги оксидира флуоридните јони до гасовит флуор (значи, флуор како проста супстанца), но последново не ја исклучува можноста за друг тип реакција меѓу HF и $KMnO_4$.

Накратко, реакцијата на HF(aq) и $KMnO_4$(s) не може да се одвива при работа со концентрирана HF(aq), со масен удел $w(\mathrm{HF}) \approx 0.4$. Сепак, реакцијата на течен флуороводород, односно HF(l) и $KMnO_4$(s) изгледа дека дава Mn_2O_7(l) кој може да експлодира дури и при умерени температури. Последново важи и за водни раствори на HF со масен удел $w(\mathrm{HF}) \geq 0.6$. Во овој прилог се објаснети некои подробности и преземени се чекори да се спречи ширење на некои мисконцепции.

Покрај ова, некои автори спомнуваат дека HF е „запалива и експлозивна“ супстанца. Ова е уште полошо отколку да се каже дека „водата е запалива и експлозивна“.

Клучни зборови: флуор; флуороводород; калиум перманганат; манган(VII) оксид;
запаливост на HF

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[*] Dedicated on the occasion of the Golden Jubilee of the *Macedonian Journal of Chemistry and Chemical Engineering*

1. INTRODUCTION

About 20 years ago, while browsing the Journal of Chemical Education, I came across one of the CLIP publications (CLIP = Chemical Laboratory Information Profile) prepared by a distinguished physical chemist J. A. Young.[1] In that publication, Young states that solid $KMnO_4$ is incompatible with "concentrated acids as HCl, HF, H_2SO_4 and others".

After reading the publication, I wrote a short comment mentioning that the incompatibility of $KMnO_4$ with HCl and H_2SO_4 is known, but with HF(aq) no reaction is expected, due to the extremely high $2F^-/F_2$ redox potential (+2.87 V), which cannot be surpassed by the Mn^{2+}/MnO_4^- potential (+1.51 V). This means that no redox reaction is possible between concentrated HF(aq) and solid $KMnO_4$.[2]

[It is worth noting that the concentration (n/V) of solid $KMnO_4$ is approximately 17 mol/l and can be easily calculated as $\rho(KMnO_4)/M(KMnO_4)$. However, at such a high concentration, the activity is significantly lower than the corresponding concentration value.]

The famous physical chemist and educator, Young, had a seemingly convincing counter argument:[2]

"Briefly put, the conclusion drawn by Petrusevski to the effect that potassium permanganate will not react with hydrofluoric acid is correct if the concentrations of the two reagents are such that these reagents are at unit activity, their temperature is 25 °C, and they are under a pressure of one atmosphere, and so on and so forth.

However, if the above conditions are not met, there may, or may not, depending upon the details, be a reaction between these two chemicals. For details describing a reaction, somewhat violent in nature, between potassium permanganate and a concentrated solution of hydrofluoric acid."[1]

From the author's reply to the comment, it appears that Young was of the opinion that $KMnO_4$ could, under certain circumstances, oxidize F^- to elemental fluorine! The comment, along with Young's brief response, was published on the same page of the Journal of Chemical Education,[2] which seemingly marked the end of the discussion for the Editor-in-Chief and the editorial team of the journal (JCE).

2. FURTHER ARGUMENTS

Later, Young and I exchanged a few private messages, where I tried to convince him that the second term (the one that is concentration dependent, i.e., the logarithmic part) in the Nernst equation $E = E^{\o} - \frac{RT}{nF} ln \frac{[\text{red}]}{[\text{ox}]}$ cannot really increase the value of the redox potential of the Mn^{2+}/MnO_4^- pair enough +2.87 V. Moreover, when we consider that concentrations should actually be replaced by activities (as mentioned above), the situation worsens!

Thus, we are left with another option for the reaction, which was described as "somewhat violent in nature" in the quoted reference.[3] I claimed that this reaction is not a redox reaction, but a "more mundane" displacement reaction, as represented by the following chemical equation:

$$KMnO_4(s) + HF(l) = KF(HF) + HMnO_4(HF) \quad (1)$$

which is immediately followed by an elimination reaction, given by the equation:

$$2HMnO_4(HF) = H_2O(HF) + Mn_2O_7(l) \quad (2)$$

The latter reaction is exothermic (due to solvation of water molecules by HF), and the resulting manganese(VII) oxide, due to the temperature increase, undergoes explosive disintegration via one of the following two possible reaction paths:

$$Mn_2O_7(l) = 2MnO_2(s) + O_3(g) \quad (3a)$$

$$Mn_2O_7(l) = 2MnO_2(s) + 1½O_2(g) \quad (3b)$$

Young partly agreed with the above, but questioned what might make the reaction described by equation (1) feasible. At first sight, the question about feasibility of equation (1) seemed a proper one. After all, HF is a much weaker acid than $HMnO_4$, so such a displacement reaction should not be possible! Generally speaking, the rule is that strong acids displace the weaker ones from their salts!

However, let us not forget that all rules have their limitations. In qualitative analytical chemistry (specifically, for cations of the second analytical group: Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, As^{3+}, and Sb^{3+}), it is well known that a weak acid can displace a stronger one. For example:

$$H_2S(aq) + HgCl_2(aq) = 2HCl(aq) + HgS(s) \quad (4)$$

We previously published a paper on this problem.[4] A similar situation occurs in a desiccator with anhydrous $CaCl_2$, containing acetic acid vapors,[5] where acetic acid displaces HCl from the drying agent, $CaCl_2$. It is, by the way, a widely spread misconception that **only** strong acids can displace the weaker ones from their salts, *quod erat demonstrandum*.

However, this logic about strong/weak acids that often applies to aqueous solutions does not necessarily apply to liquefied HF (or HF-rich aqueous solutions). On the other hand, liquid HF does have a property in which it resembles concentrated sulfuric acid: a piece of filter paper is momentarily carbonized upon contact with liquefied HF, obviously due to the elimination of water from cellulose. This tells us something about its dehydration properties, which are directly comparable with the strongest drying agents, including P_2O_5 and H_2SO_4. In fact, liquid HF resembles concentrated H_2SO_4 in several respects.

For example, the reaction of concentrated H_2SO_4 and solid potassium permanganate proceeds according to the chemical equations:

$$H_2SO_4(l) + KMnO_4(s) = HMnO_4(H_2SO_4) + \\ + KHSO_4(H_2SO_4) \quad (5)$$

The first product immediately undergoes a secondary reaction (cf. equation 2):

$$2HMnO_4(H_2SO_4) = H_2O(H_2SO_4) + Mn_2O_7(l) \quad (6)$$

Finally, manganese(VII) oxide is subject to an explosive disintegration reaction, described according to one of the two reaction pathways illustrated in equations 3a or 3b.[6]

3. ON FLUORINE GENERATION

The only practical method of generating fluorine in quantities remains electrolysis, basically in the way it was first isolated by Moissan in 1886*, but using modified vessels of nickel, copper, or their alloys instead of the more expensive platinum and iridium vessel.[7] Unfortunately, it is not possible to oxidize HF in any other way but by electrolysis (e.g., electrolysis of molten $KF\cdot n HF$ or similar systems). If there were another way, we could hopefully find some information in the rich chemical literature on permanganates as oxidizers.[8 and the references therein] This fact, however, does not prevent the generation of fluorine on a small scale by chemical methods, the so-called fluorine synthesis,[9] which is a truly ingenious process. But that is another story.

4. MOTIVATION FOR THE PRESENT WORK: FIGHTING POSSIBLE MISCONCEPTIONS

One could wonder why do I go back two decades and mention all that happened? After all, Jay A. Young died 13 years ago and cannot comment on or reply to my reflections. Most probably, I would have remained silent had I not come across several websites mentioning the oxidation of HF with $KMnO_4$, with the balanced reaction equation.[10,11] I suspect the authors' intention was to teach readers how to balance redox reactions, but the choice of the system was terribly unfortunate. What is possible with HCl(aq) appears to be impossible with HF(aq).

Thus, one of the favorite methods for generation of chlorine is oxidation of hydrochloric acid by potassium permanganate, but the analogous reaction with HF(aq) is impossible, as is any redox reaction between permanganate and HF(l).

When encountering online sources that include equations describing reactions between hydrofluoric acid and potassium permanganate, one may come across potential sources of misconceptions for young chemists. These misconceptions must be revealed and made clear to chemistry teachers, with an aim to prevent the spread of misconceptions (by definition: misconception is an idea that is wrong because it is based on a failure to understand a situation).[13]

There is yet another misconception regarding HF in both chemistry literature and other sources: the claim that HF is "flammable and explosive".[12] This is as unbelievable as saying that water is flammable and explosive. The above comparison is quite appropriate: water is a product of burning hydrogen in oxygen, just as HF is the product of burning hydrogen in fluorine.

In this particular case, the source of the misconception (likely a local one, as it seems to be an isolated belief of the author of reference 12 about "flammable and explosive HF" could stem from: (a) a simple misunderstanding. It is often mentioned that liquefied HF is a fuming liquid and if English is not your native language it is easy to mix/interchange "flammable" and "fuming". Also, there is an old saying "When you see fumes, there must be fire somewhere", which could have contributed to the spread of this misconception; (b) If the authors are not chemists (in the cited paper the author is probably a physicist and is of Russian

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[*] In 1907 Moissan was awarded the Nobel Prize in chemistry for the isolation of fluorine as a simple substance. There were two candidates (Moissan and Mendeleev) and Moissan won by a margin of just one vote! A few months later, Moissan died from appendicitis, although there was a speculation that repeated exposure to fluorine and carbon monoxide also contributed to his death.

Life was not fair to Mendeleev too, for he died the very next year. Thinking about it, it seems to me that the Nobel Committee had several chances even earlier (1902 – 1905) to award Mendeleev for his historical discovery of the periodicity law, but they seemingly did not value the discovery… or, perhaps, there were some other reasons!

nationality), there may be more possibilities for misunderstandings.

The author writes about the properties of HF, "It dissolves well in water but is flammable and explosive."[12] The end of the quote is completely wrong. While liquid HF may explode upon mixing with incompatible chemicals, it is neither flammable nor explosive by itself!

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