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Education

DEMONSTRATIONS AS A TOOL FOR IRONING-OUT MISCONCEPTIONS:
1. ON THE CATALYTIC REDUCTION OF POTASSIUM PERMANGANATE SOLUTION WITH ATOMIC HYDROGEN

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It has been known that the reduction of permanganate solution with atomic hydrogen is much faster in the presence of nitrate ions. A possible explanation for this phenomenon was offered some time ago [1]. This explanation was checked by a planned experiment that proves it to be a misconception. Two other possibilities were offered one of which is in agreement with the results of both the demonstration, and the planned experiment.

Key words: general chemistry; chemical demonstrations; misconceptions; catalysis, reduction; atomic hydrogen; permanganate

INTRODUCTION

Demonstration experiments (demonstrations) are of key importance in teaching sciences. They are perhaps even more important in pure chemistry, due to the fact that one may in principle 'activate' all senses in the process of perception of the results of chemical experiments. Demonstrations should be relatively short (5–10 min is an optimum duration), performed with the simplest equipment that ensures the same effect and it is vital that the chemistry behind them is well understood.

An important general chemistry topic that is covered with a variety of demonstrations is catalysis. In searching for an appropriate heuristic experiment on catalysis, one finds the following simple and effective example [2]: two identical demonstration test tubes contain the same volume (e.g. 50 mL) of diluted sulfuric acid and some potassium permanganate solution (previously added to the acid). A small amount (say 2 mL) of KNO_3 solution (c = 1 mol/L) is added to one of the test tubes. Upon addition of zinc metal (the same quantity, say 3 g, is added to both test tubes), hydrogen gas is briskly evolved. After 1–2 min, the solution in the tube containing KNO_3 becomes colourless, while the discoloration of the other tube takes about 15 min or even longer (cf. Fig. 1).

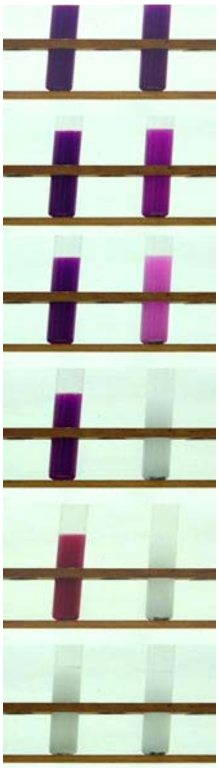

Fig. 1. Chemical changes in the system H_2SO_4(aq)–Zn(s)–$KMnO_4$(aq) in the absence (left) and in the presence (right) of KNO_3(aq). Duration of experiment increases on going from top to the bottom

Obviously, KNO_3 acts as a catalyst. An independent check was done and proved that other nitrate salts may be used as well. The catalytic action thus results from the presence of nitrate anions.

The chemical changes *in the absence* of catalyst are usually explained in terms of the permanganate solution being reduced by the action of atomic (or nascent) hydrogen that is formed in a low concentration by the reaction of sulfuric acid and zinc:

$$Zn(s) + H_2SO_4(aq) = 2H(aq) + ZnSO_4(aq) \quad (1)$$

$$5H(aq) + 3H_3O^+(aq) + MnO_4^-(aq) =$$
$$= Mn^{2+}(aq) + 7H_2O(I) \quad (2)$$

However, nothing was said [2] about the chemical changes in the system *in the presence* of the catalyst.

The purpose of the present paper was to enlighten the chemical changes in this relatively simple system. Since this experiment (and the explanation as well) is suitable as a good heuristic experiment to catalysis, it would be more than appropriate to offer an explanation in terms of some simple chemical reasoning (relying on some well known facts from general & inorganic chemistry). This should then be followed by correspondingly simple chemical experiments/demonstrations that would serve as a proof to the offered explanation.

Possible Explanation: Our First Conjecture

Few years ago [1], we offered an explanation that seemed to be in line with the above observations. The reasoning was as follows: one may consider the reaction system as containing sulfuric and very diluted nitric acid (since all nitrates are soluble in water and are present in anionic form). Knowing that the action of diluted nitric acid on various metals is usually followed by liberation of NO, one comes to the following conjecture for the chemical reactions in the system containing nitrates as a catalyst:

$$3H(aq) + NO_3^-(aq) + H_3O^+(aq) =$$
$$= NO(aq) + 3H_2O(l) \quad (3)$$

$$5NO(aq) + 4H_3O^+(aq) + 3MnO_4^-(aq) =$$
$$= 5NO_3^-(aq) + 3Mn^{2+}(aq) + 6H_2O(l) \quad (4)$$

The above notion (concerning the chemical reactions taking place) was further strengthened by an additional experiment, showing that NO gas is indeed slowly consumed in an acidified $KMnO_4$ solution [1]. Although it is not a direct evidence for the proposed chemical changes, one could at least say that the experimental results are not in disagreement with them. The authors were careful enough [1] as to mention that it is possible that the proposed conjecture is not necessarily correct.

During the course of further work, devoted mainly to chemical demonstrations and experiments as a possible tool for ironing-out misconceptions [3], we came across the idea for a more decisive planned experiment, as a more thorough independent check for the correctness of the proposed explanation.

Independent Check:
Planned Experiment and Results

Providing the offered explanation is correct, the small amount of NO (most probably dissolved in the water, despite its rather low solubility) reduces the permanganate and is oxidised back to nitrate. Hence, the initial and final amount of nitrate ions is the same. In short, this means that the catalyst is quantitatively recovered. Two important questions can crop here:

(a) *What is expected if the initial solution does not contain any permanganate?*

If indeed NO is generated (as an intermediary compound, in the process of catalysis), in the absence of permanganate no back oxidation could occur. In other words, NO will start to accumulate and one may expect (after a while) that, due to its low solubility in water, saturation will soon be reached. Once saturation is attained, evolution of NO gas is inevitable:

$$NO(aq) = NO(g) \quad (5)$$

The gas will of course escape, thus leading to nitrogen depletion. In principle, NO will further be readily oxidised by air oxygen:

$$2NO(aq) + O_2(g) = 2NO_2(g) \quad (6)$$

Still, if present only in low concentrations, the product (under normal conditions a brown gas) could remain undetected. Anyway, under the above experimental conditions (i.e. in the absence of oxidiser) the system will be nitrogen depleted, as explained above.

(b) What is to be expected if the contents of this system (the liquor) is added to a potassium permanganate solution?

If the offered explanation about the chemical changes in the presence of catalyst is correct, due to the nitrogen (or NO) depletion one actually expects no reaction! The permanganate solution should retain its colour. In case of discoloration, however, one would have to conclude that the offered explanation (based on NO_3^- reduction and formation of NO) is definitely a wrong one.

The corresponding planned experiment was performed as follows: four beakers (100 mL beakers work fine) were placed on a styrofoam block. The outer beakers contain metallic zinc and sulfuric acid. Small amount (1 mL) of KNO_3 solution was added to the rightmost one. The inner beakers contain $KMnO_4$ solution. After few minutes, the liquor of the outer beakers was decanted and kept for further use (cf. Fig. 2 a).

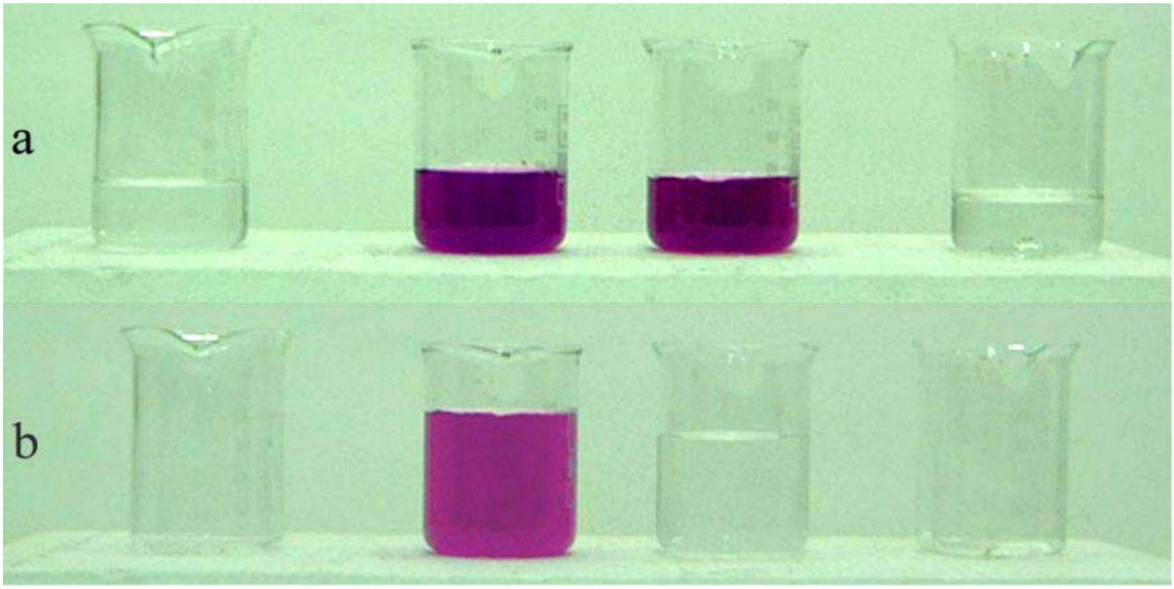

Fig. 2.(a) The contents of the liquor decanted from the rest of the reaction system in H_2SO_4(aq)–Zn(s) (outer left) and H_2SO_4(aq)–Zn(s)–KNO_3(aq) (outer right) is added to the neighbouring permanganate solution (b)

The liquor from the outer beakers was then added to the neighbouring inner beakers containing permanganate solution. The liquid in the inner right beaker is immediately discoloured! No changes occur in the liquid of the inner left beaker (cf. Fig. 2 b). It is thus beyond any doubt that the offered explanation based on NO formation is wrong and must be avoided. Further, a modified explanation is needed, one that will take into consideration the results of the planned experiment.

Possible Options for a New Explanation

Obviously, no formation of a gaseous reducing product is possible. Considering the system in question, one could assume that the diluted nitric acid is reduced to nitrous acid:

$$2H(aq) + HNO_3(aq) = HNO_2(aq) + H_2O(l) \quad (7)$$

Nitrous acid is an efficient reducing agent of the permanganate solution:

$$5HNO_2(aq) + 2MnO_4^-(aq) + H_3O^+(aq) = 5HNO_3(aq) + 2Mn^{2+}(aq) + 4H_2O(l) \quad (8)$$

This possible explanation is still a conjecture (albeit a better one), unless a more direct evidence for the presence of nitrous acid in the reaction product is given. One way to do this is to check whether the liquor has properties of a strong oxidiser, because diluted HNO_2 is known to be a really strong oxidising agent – much stronger than nitric acid of the same concentration [4]. As a powerful oxidiser, HNO_2 momentarily oxidises solutions of iodides, to give black (or brown, depending on the concentration) product – iodine as simple substance

Part of the liquor of the rightmost beaker (cf. Fig. 2 a) was added to the water solution of KI. No reaction occurred! Unequivocally, this proves that no nitrous acid in any form is present in the system.

Nitrates are therefore reduced by atomic hydrogen to give fairly strong and relatively stable reducing agent. There are many possible products that can be obtained upon reduction of nitric acid/nitrates. They are listed in the order of decreasing the oxidation number of the nitrogen: NO_2, HNO_2, NO, $H_2N_2O_2$, N_2O, N_2, NH_2OH, N_2H_4, NH_3. Two of them are known as strong reducing agents: hydrazine (N_2H_4, the most powerful one), and hydroxylamine (NH_2OH). The nature of the product depends on the acid (or nitrate ions) concentration, the used reducing agent and the pH value at which reduction takes place.

After reviewing few textbooks of inorganic chemistry, one finds [5] that during electrolysis of nitric acid, the nascent hydrogen (at the cathode) is capable of producing hydroxylamine:

$$HNO_3(aq) + 6H(aq) = NH_2OH(aq) + 2H_2O(l) \quad (9)$$

Hydroxylamine can, therefore be the 'intermediate product' during the catalysis. In our example, it is reasonable to expect that (due to the excess of sulfuric acid present) the hydroxylamine will be protonated to give $(NH_3OH)_2SO_4$. This, however, must be confirmed in some way, otherwise it will be one more conjecture.

The liquor was first neutralised with KOH, and then was added to ammoniated silver nitrate solution. After few seconds, grey precipitate of metallic silver is formed (cf. Fig. 3). This proves that strong reducing agent is indeed present in the solution, and it *could be* due to the hydroxylamine (hydroylammonium sulfate) present.

However, there is also another possibility that the strong reducing agent might be hydrazine (i.e. hydrazinium sulfate), although it would be somewhat strange to be synthesised in the above way. Anyway, further check of the neutralised reaction liquor was performed, this time with ammoniated copper sulfate solution. If hydrazine in any form was present in the liquor, one should expect reduction of Cu^{2+} ions to occur with appearance of either a copper mirror, or dark precipitate [6]. At the very least, the loss of the intense blue colour of the $[Cu(NH_3)_4]^{2+}$ complex cations would indicate presence of hydrazine. No reaction occurred this time. The conclusion is that, in the presence of nitrate ions (i.e. diluted nitric acid), the atomic hydrogen generated in the reaction of zinc and sulphuric acid gives hydroxylamine, and this is immediately protonated in sulphuric acid medium to give hydroxylammonium sulfate (i.e. hydroxylammonium ions). Hydroxylamonium ions are efficient reducing agent, and discoloration of $KMnO_4$ solution occurs much faster than in the absence of nitrate ions (i.e. when no KNO_3 is added).

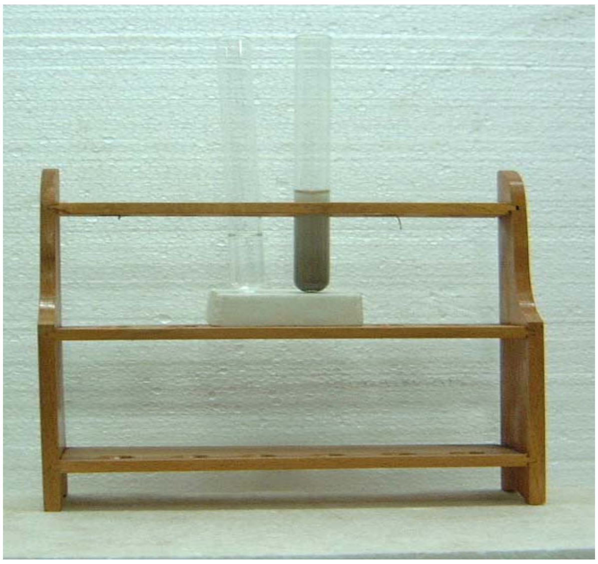

Fig.3. Liquors from outer-left and outer-right beakers (cf. Fig. 2) are added to the left and right test tube correspondingly, both containing ammoniated $AgNO_3$ solution. Grey precipitate of silver is evident in the right test tube, thus indicating a presence of a strong reducing agent formed by reduction of nitrate ions

As mentioned in the beginning, all of the above came as a result of simple chemical reasoning. Only simple/readily available equipment was used.

Safety Tips

Safety goggles should be worn at all times while performing chemical demonstrations.

Sulfuric acid (even diluted) is toxic and corrosive agent and must be handled with care. The concentrated acid is highly hygroscopic. Dilution of sulfuric acid must be done according to safety regulations (see for example ref. [7] and the references therein).

Concentrated ammonia solution is corrosive and must also be handled with care. Note that ammonia vapours are slightly toxic, irritating and have rather unpleasant smell.

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Резиме

ДЕМОНСТРАЦИОНИТЕ ЕКСПЕРИМЕНТИ КАКО СРЕДСТВО ЗА КОРЕКЦИЈА НА ПОГРЕШНИ ПРЕТСТАВИ:

1. ЗА КАТАЛИТИЧКА РЕДУКЦИЈА НА РАСТВОР ОД КАЛИУМ ПЕРМАНГАНАТ, СО НАСЦЕНТЕН ВОДОРОД

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Клучни зборови: општа хемија; демонстрациони експерименти; погрешни претстави; катализа, редукција; насцентен водород; перманганат

Познато е дека редукцијата на раствор од калиум перманганат со насцентен водород се одвива многу побрзо во присуство на нитратни јони. Пред извесно време беше понудено можно објаснение за овој феномен [1]. Извршената проверка на понуденото објаснение, со планиран експеримент, покажува дека се работи за погрешно толкување, односно погрешна претстава. Уште две други можности се разгледани, од кои едната е во согласност со резултатите и од демонстрацијата и од планираниот експеримент.