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How to Predict a Chemical Reaction – Pourbaix Diagrams as a Tool to Visualize pH-dependent Redox Reactions

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Abstract

Reactions involving proton-coupled electron transfers (PCET) are key processes for the transformation toward a more sustainable industry. These include water electrolysis[1], electrochemical nitrogen fixation[2], and the reduction of carbon dioxide into useful synthetic building blocks[3]. The interdisciplinary collaborative research center (CRC 1633), coordinated by the University of Göttingen, is dedicated to understanding the principles of PCET and its correlation with electronic structure, as well as exploring potential pathways for the rational design of future electrocatalysts. Although this is fundamental research, which can be challenging to communicate briefly, it provides the opportunity to highlight the potential and benefits of electrocatalysis.
In this field, Pourbaix and Pourbaix-type diagrams are frequently used to describe electrochemical systems involving proton and electron transfers without requiring the use of the Nernst equation. Exercises based on these diagrams allow the combination of two major examples of the donor-acceptor principle in school curricula: proton transfer in acid/base reactions and electron transfer in redox chemistry. In this contribution, we present an experiment that correlates the pH-dependent redox behavior of manganese species with an appropriate Pourbaix diagram.
This experiment, including short exercises, was part of an internship for upper secondary level school students at Göttingen University. The station was themed "How to predict a chemical reaction?" to spark student interest and consists of three steps: First, students perform the reduction of Mn(VII) with iodide to Mn(II) at pH 0 and Mn(VI) at pH 14. The distinct colors of the species allow the students to correlate their observations with a Pourbaix diagram, identify the reduced species, and predict the reaction product at pH 7 to be brown manganese dioxide, which was experimentally confirmed afterwards. The contribution concludes with a brief evaluation of how well the students applied their knowledge of pH-dependent redox reactions and adapted Pourbaix diagrams to predict reactions in the Mn/Br system.

Keywords: *Science Outreach, PCET, Redox Chemistry, Pourbaix diagram*

1. Introduction

The redox potential of reactions involving protons depends on the pH value of the reaction medium. This is expressed in the Nernst equation where protons are included as reaction components like all other species. However, this complicates the equation itself and can potentially make the concept of concentration dependence harder to grasp for students. Therefore, in some cases the protons are omitted when formulating the Nernst equation, for example in the curriculum of the German state of Lower Saxony[4]. Despite this, for some reactions potentially carried out in chemistry class, some students will observe the pH-dependent reduction product of potassium permanganate which include colorless Mn^{2+} or dark brown MnO_2.

To reflect this behavior without the need to unnecessarily complicate the Nernst equation, so called Pourbaix diagrams can be used. Although they can be constructed from the complete Nernst equations for all considered reactions in conjunction with additional information like solubility constants, for most relevant redox systems they can be found in literature[5].
The use of Pourbaix diagrams enables the students to determine whether a chosen redox reaction is possible under the given condition or even graphically evaluate which reaction is most favorable if more than one different reaction is thermodynamically possible. Moreover, due to their descriptive nature of complex circumstances, they are also used as a tool in research. Pourbaix-type diagrams are especially useful to describe so-called proton-coupled electron transfers, although mostly in a modified form, where the pK_a value is used instead of pH.

One prominent example of current PCET research is the reduction of elemental nitrogen to ammonia (nitrogen fixation). The product ammonia is one of the most important commodity chemicals, mainly used for the production of fertilizers. The conventional synthesis using the Haber-Bosch process involving hydrogen produced by steam reforming is responsible for more than 1% of the total global carbon dioxide emissions, making a more sustainable alternative process very instrumental to fight climate change. One possible solution is the use of electrosynthesis powered by renewable energies but this comes with great challenges for interdisciplinary research: Thermodynamically, the reduction of water to gaseous hydrogen is more favorable in most cases than the production of ammonia which can be shown using an appropriate Pourbaix diagram. To overcome this, the rational design of electrocatalysts which favor the desired reaction over possible side reactions plays an important role in current electrochemistry research.

We are convinced that Pourbaix diagrams can be used as valuable tool in chemistry class and internships to visually teach pH-dependent redox potentials combined with a unique opportunity to connect this knowledge to fundamental research.

2. Internship in Chemistry for School Students at University of Göttingen

The University of Göttingen offers an annual three-day internship for school students in grade 11 and 12 aimed to raise interest in chemistry for vocational orientation purposes. During this internship, the students will experience practical lab courses in organic, physical and inorganic chemistry. In fall 2024, the inorganic chemistry part was conducted in cooperation with CRC 1633 to both provide hands-on experience on laboratory techniques like filtration, electrolysis, heating and cooling as well as insights into PCET research and the fundamental question this CRC is dedicated to answer.
The internship was conducted as a station learning session, where a total of 13 stations was available for the students to choose from. On every station, the participants can perform one experiment, ranging from visually impressive reactions such as the synthesis and combustion of pyrophoric iron to electrolysis and fuel cells or the electrobromination of organic dyes as examples how chemistry contributes to a sustainable future. Every experimental station is accompanied with an explanatory text and a short introduction is given by students or lab technicians before the participants started to experiment on their own. This contribution is about a short series of experiments and related tasks presented to the school students themed as “How to predict an electrochemical reaction?”. Therefore, experiments regarding the manganese system were chosen, since the corresponding Pourbaix diagram involves a variety of species with distinct colors.

2.1 Didactical Perspectives of Pourbaix Diagrams

In general, Pourbaix diagrams are graphical representations of the redox potential for a given system. The stability ranges of all occurring compounds are therein separated by straight lines and can be colored in order to match the appearance of the species itself (see Figure 1 for the manganese system). The slope of these lines is calculated using the Nernst equation, leading to the differentiation of three cases:

(1) Horizontal lines: No protons are involved in a reaction crossing this line, meaning the redox potential does not depend on the pH value. One example might be the oxidation of manganese metal to Mn^{2+} ions.
(2) Vertical lines: No electron transfers (oxidation, reduction) are involved in a reaction crossing this line, meaning the reaction only depends on the pH value. One example might be the precipitation of manganese hydroxide from an alkaline solution of Mn^{2+} ions.
(3) Diagonal lines: Both electrons and protons (or hydroxide ions) take part in a reaction crossing this line, meaning the redox potential is influenced by the pH value. One example might be the precipitation of manganese oxide hydroxide (MnO(OH)) from a Mn^{2+} solution at a redox potential of around 0.4 V and neutral pH, were both the oxidation state changes from Mn(II) to Mn(III) and hydroxide ions are involved.

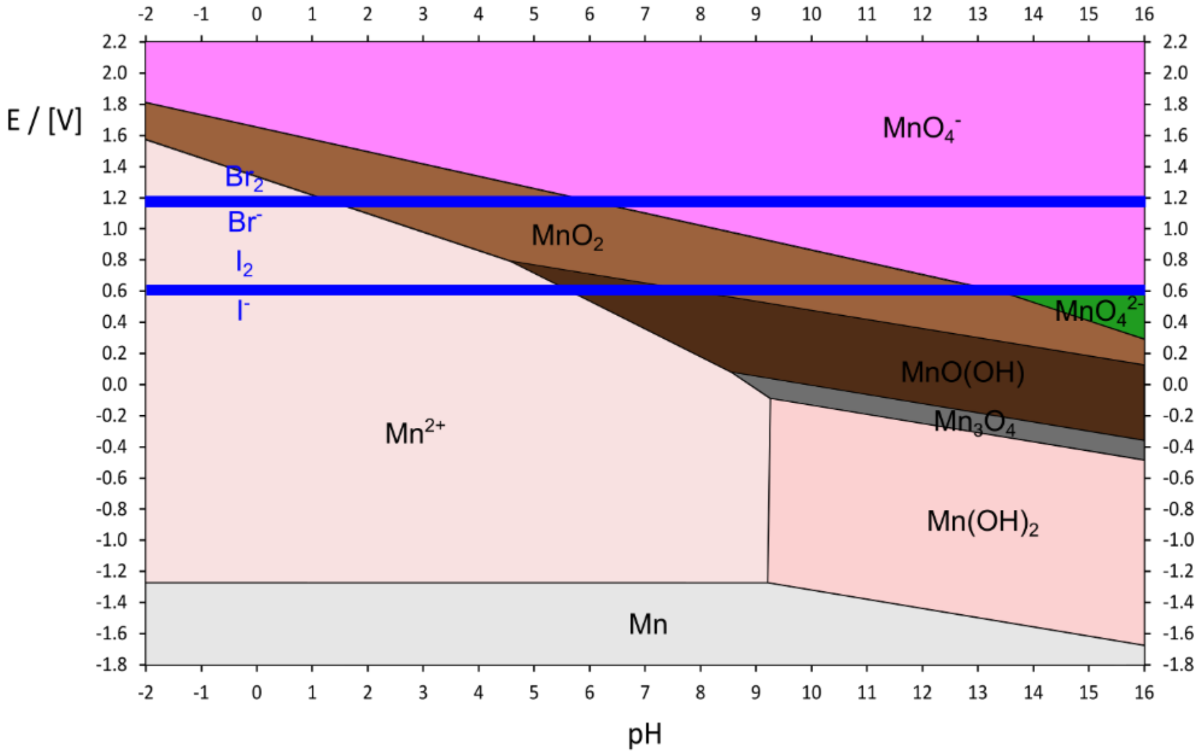

Fig. 1. *Pourbaix diagram of manganese species in an aqueous system under ambient conditions with added potentials of the Br_2/Br^- and I_2/I^- redox couple. All values calculated according to [9,10].*

Such a diagram displaying the stability ranges of all covered species can be used to predict reactions when combined with the redox potential of given oxidizing or reducing agent. In our case, we have selected the I_2/I^- and Br_2/Br^- systems, respectively, since their redox potential does not depend on the pH value and can be shown by a straight horizontal line. If the identification or prediction of the thermodynamically stable manganese species in the presence of I_2/I^- at pH ~ 0 is desired, one could simply find the intersection of the redox potential defined by the redox couple I_2/I^- (~ 0.6 V) and the given pH value, resulting in Mn^{2+} ions to be found as the stable species. This also implies that this ion would also be the reaction product of any given manganese species at this pH value if a 1:1 mixture of iodine and iodide is used. To avoid handling large amounts of halogens in our experiments, we will only consider the reduction reaction of the most oxidized manganese species (permanganate, MnO_4^-) with the respective halide as reducing agent. Applied to the Pourbaix diagram given in Figure 1, one has to search for the most stable species by starting from the top and moving down until the line of the respective reducing agent is intersected. In order to compensate for concentration changes of reducing agent upon reaction, the respective potentials are drawn as broad lines to cover a potential range.

In the first place, Pourbaix diagrams were developed as a graphical representation to evaluate the corrosion resistance of metals under specific conditions. By combining such diagrams with the lines corresponding to the redox potential of oxygen and/or water, respectively, one can easily observe, whether a metal is stable against corrosion at the pH value given by the desired application. It has to be kept in mind that these diagrams and the underlying Nernst equation only take thermodynamics into account, meaning that e.g. aluminum will be considered unstable in air and pure water. However, this finding can be used as a leaning opportunity to introduce the concepts of (thermodynamic) immunity and (kinetic) passivation due to protective layers.

For educational purposes, Pourbaix diagrams were mainly considered useful for undergraduate university education, where they can help to link the thermodynamic calculations of potential, pH, equilibrium constant, concentration, and changes in Gibbs energy to experimental observation and results or focusing on the aspect of corrosion resistance and protection.[6-8]

2.2 Experimental Procedure and Tasks

Before the experiment begins, the students were given basic information on the pH-dependence of redox systems and the differentiation between kinetics and thermodynamics. Afterwards, they continued with the experiments: First, they prepared three 25 mL beakers with 2 mL of 0.01 M potassium iodide solution and added another 8 mL of 1.0 M hydrochloric acid solution, demineralized water and 1.0 M sodium hydroxide solution, respectively.
After adding 2 mL of 0.005 M potassium permanganate solution to the acidic (pH ~ 0) and alkaline (pH ~ 14) solution (Figure 2, left and right), the students were asked to monitor the color changes and find correlations to the provided Pourbaix diagram with a prominently drawn I^-/I_2-line (Figure 1). This diagram not only shows the thermodynamical stable species for each given condition but also its chemical formula. Due to the heterogeneity of the group, some advice was given if needed. All student groups were able complete this task and thereby identify the species as Mn^{2+} and MnO_4^{2-}, respectively, although with different need for support

$MnO_4^- + 8\ H_3O^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 12\ H_2O$ (eq. 1)
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$ (eq. 2)

Their next task was to use this knowledge to predict the reaction product at pH 7, conduct the experiment afterwards and to confirm their prediction with the observation. In this case, there was also some support needed for some of the groups. However, the formation of brown oxide hydroxide (mor manganese dioxide to simplify the reaction) (Figure 2, center) could be confirmed by all participants.

$MnO_4^- + 3\ e^- + 2\ H_2O \rightleftharpoons MnO_2 + 4\ OH^-$ (eq. 3)

Fig. 2. *Reaction mixture of $KMnO_4$ and KI in strongly acidic, neutral and strongly basic medium, respectively (left to right).*

3. Experiences and Questionnaire

The students were very motivated to choose the presented experimental station from the variety of offers. We attribute this, in part, to the title which is about the prediction of a chemical reaction. Although none of the students was aware of pH-dependent redox potentials in the first place, they were familiar with redox reactions being electron transfers. Overall, they could follow the explanations regarding the need for choosing the best reaction conditions for a given reaction and were curious about how (electro)catalysts can favor one possible reaction compared to side reactions.

In order to assess whether the principles of pH-dependent redox potentials and the use of Pourbaix diagrams can be successfully used in lab courses with upper secondary level school students, a brief questionnaire with ten students was conducted. Therefore, the students were asked to answer three multiple choice questions, where it was clearly stated that only one answer has to be marked. These questions tasked them with the reproduction of conceptual knowledge of pH-dependent redox reactions given in the introductory text and the information given by the instructor as well as another prediction of the product of chemical reaction (Potassium permanganate with potassium bromide at pH 12), which could be answered using the provided Pourbaix diagram. The questionnaire translated from German is given in Figure 3. Overall, the majority of students could answer the given questions correctly. In total, 21 from 29 given answers were correct and only one student gave no answer to question 1. Most of them could differentiate that a Pourbaix diagram does not allow for the determination of reaction kinetics (questions 1 und 2) and could also successfully predict that no reaction will occur under the conditions given in question 3.

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Questionnaire

Question 1: Which statement is correct?

( ) Every chemical reaction is faster in acidic medium (low pH value).
( ) Every chemical reaction is faster in basic medium (high pH value).
( ) The product of reactions involving protons (H^+ ions) depends on the pH value.
( ) The product of reactions involving electrons (e^-) depends on the pH value.

Question 2: Which statement is not correct?

A Pourbaix diagram can be used to determine...
( )... whether oxidizing and reducing agent will react which each other at a given pH value.
( )... to which product the oxidizing and reducing agent will react at a given pH value.
( )... how fast oxidizing and reducing agent will react at a given pH value.

Question 3: To which product will permanganate ions (manganate(VII), MnO_4^-) and bromide ions (Br^-) at pH 12?

( ) Manganese(II) hydroxide, $Mn(OH)_2$, brown
( ) Manganese(IV) oxide, MnO_2, brown
( ) Manganate(V), MnO_4^{3-}, blue
( ) There will be no reaction at all. Permanganate (violet) and bromide (colorless) remain unchanged.

Fig. 3. *Questionnaire for evaluating the experimental station “How to predict an electrochemical reaction?” translated into English.*

4. Conclusion and Outlook

A short experimental series with the MnO_4^-/I^- system taking about 10 minutes was successfully conducted within the internship for upper level secondary school students. With the given procedure, we achieved a safe and reproducible experimental setup where the observation correlated well with the constructed Pourbaix diagram. These experiments were used to introduce the students from Lower Saxony with the concept of pH-dependent redox potentials which is not part of the respective school curriculum.
The colorful reaction raised the interest of the participants and was very well suited to explain why fundamental research on electrochemistry, more specifically proton-coupled electron transfer, can play an important role for more sustainable processes. In particular, both nitrogen fixation and carbon dioxide reduction and the associated need for specifically designed catalysts to suppress their common unwanted side reaction of hydrogen evolution are suitable examples to emphasize the importance of interdisciplinary research.

The experiments have to be further evaluated with a larger group of participants but yet promise great potential to be developed further for broader target audiences: (1) The extended use of typical lab equipment like automatic pipettes and magnetic stirrers can make them visually more attractive for future internships and (2) a more in-depth course for experimental school laboratories or undergraduate university studies can work out the connection between Pourbaix diagrams and the

Nernst equation, ultimately leading to the construction of a Pourbaix diagram which can be experimentally confirmed.

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