

Some Applications of Latimer Diagrams in Teaching Oxidation-Reduction Reactions for Chemistry Students at Pedagogical Universities

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Abstract In the training program for chemistry pedagogical students at pedagogical universities, knowledge of oxidation-reduction reactions is taught when students learn about the electrochemistry chapter belonging to the theory of chemical processes. There, students are introduced to how to use standard electrode potential values of oxidation/reduction pairs to predict the likelihood of an oxidation-reduction reaction. However, a common difficulty for students is predicting reaction products of substances containing elements with several oxidation states. To simplify this problem, using the Latimer diagram will help students be more interested in predicting the stable oxidation state of the element, calculating the standard reduction potential of oxidation-reduction pairs that are not close to each other and predict the products of many complex oxidation-reduction reactions.

Keywords: Latimer diagram, standard electrode potential, standard reduction potential, oxidation-reduction reactions, teaching chemistry

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1. Introduction

1.1. Latimer Diagram

This is one of the potential data diagrams summarizing the relative thermodynamic stability of a series of compounds of the same element in different oxidation states [1,2,3,5]. The author of the diagram is Wendell Mitchell Latimer, an American chemist, one of the leaders in the application of thermodynamics in inorganic chemistry [13]. The Latimer diagram is a simple and convenient way to record the oxidation-reduction properties of an element representing many different oxidation numbers. From left to right, the elemental compounds are arranged in order of decreasing oxidation number [4,6].

The diagram is denoted [1,7,8]:



Where:

Oxid and Red are the oxidized and reduced forms of the reduction half-reaction.

 $\pm m$ and $\pm n$ is the oxidation number of the element.

 E° is the standard reduction potential of that half-reaction (unit is V).

Example: The symbol:

$$^{+7}{\rm ClO_4^-}$$
 $\xrightarrow{+1.20}{\rm V}$ $^{+5}{\rm ClO_3^-}$

means corresponding to the half-reaction:

$$ClO_4^- + 2H^+ + 2e \longrightarrow ClO_3^- + H_2O E^o = +1.20 V$$

The symbol:

means corresponding to the half-reaction:

$$2\text{HClO} + 2\text{H}^+ + 2\text{e} \longrightarrow \text{Cl}_2 + 2\text{H}_2\text{O} \text{E}^\circ = +1.63 \text{V}$$

In addition, based on Hess's law, we can establish a Latimer diagram to compare the standard reduction potentials of the reactants and products of the reaction, thereby making predictions about the favorable direction of the reaction.

1.2. Latimer Diagram of Some Elements

The electrode potential data are quoted from references [9,10,11,12,13,14].

Subgroup IA

Acidic solution:



Basic solution:



Subgroup IIA

Acidic solution:

+2
 0

$$Be^{2^+}$$
 -1.850 V
 Be

 Mg^{2^+}
 -2.356 V
 Mg

 Ca^{2^+}
 -2.840 V
 Ca

 Sr^{2^+}
 -2.890 V
 Sr

 Ba^{2^+}
 -2.920 V
 Ba

 Ba^{2^+}
 -2.916 V
 Ra

Basic solution:

Basic solution:



Subgroup IIIA Acidic solution:









Subgroup IVA



Subgroup VA





Basic solution:

Subgroup VIIIA



Basic solution:

Subgroup IIB

Acidic solution:



Basic solution:

+2 0

$$Zn(OH)_4^2$$
 - - 1.285 V Zn
 $Zn(OH)_2$ - - 1.246 V
 $Cd(OH)_2$ - 0.824 V Cd
HgO + 0.098 V Hg

Subgroup VIB





Basic solution:



Subgroup VIIIB

Acidic solution:



2. Content and Research Methods



2.1. Predict the Stable Oxidation State of the Element

Consider the two half-reactions side by side in the Latimer diagram:

If E^o_{B/C} > E^o_{A/B} then half of the reaction of the B/C pair proceeds spontaneously in the forward direction and the other half A/B in the reverse direction → B is an unstable particle, it has the

ability to self-oxidize-reduce to A (higher oxidation number) and C (lower oxidation number). That process is called disproportion.

• If $E^{\circ}_{B/C} < E^{\circ}_{A/B}$ then half of the reaction of the B/C pair proceeds spontaneously in the reverse direction and the other half A/B in the forward direction \rightarrow B is a stable particle, particle A (higher oxidation number) will react with particle C (lower oxidation number) to produce B (intermediate oxidation number). That process is called comproportion.

Note: The standard reduction potential written on the hyphen corresponds to the half-reaction going from left to right (forward direction). When writing in the reverse direction, pay attention to changing the sign of the standard reduction potential.

Example 1: From the Latimer diagram for oxygen (see subgroup VIA), we see that H_2O_2 is unstable in acidic solution and is disproportioned into H_2O and O_2 .

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \qquad E^o = + 1.763 V$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e \qquad E^o = - 0.695 V$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad E^o = + 1.068 V$$

The total reaction potential is quite positive, so the reaction is thermodynamically favorable. In fact, H_2O_2 decomposes immediately under normal conditions, but occurs at a very small rate, not clearly observed. When there is a catalyst or when heated or exposed to light, the reaction occurs very quickly, sometimes causing an explosion.

Example 2: From the Latimer diagram for iron (see subgroup VIIIB), we see $E^{o}_{Fe^{3+}/Fe^{2+}} > E^{o}_{Fe^{2+}/Fe}$, that is, Fe^{2+} is stable to disproportion, while Fe^{3+} and Fe undergo comproportion, that is, they will interact with each other to produce Fe^{2+} . This result is confirmed, by calculating the sum of the following two half-reactions:

$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+} \qquad E^{o} = \pm 0.77 V$$

$$Fe \longrightarrow Fe^{2+} + 2e \qquad E^{o} = \pm 0.44 V$$

$$2Fe^{3+} + Fe \longrightarrow 3Fe^{2+} \qquad E^{o} = \pm 1.21 V$$

The total reaction potential is quite positive (+ 1.21V), so the comproportion occurs easily in aqueous solution.

2.2. Calculate the Standard Reduction Potential of Oxidation-Reduction Pairs that are Not Close to Each Other

Another application of the Latimer diagram is that from the diagram it is possible to calculate the standard reduction potential of oxidation-reduction pairs that are not close to each other. The calculation is based on the relationship between ΔG° and E° of the process and the reality is common ΔG° of n successive processes is equal to the sum ΔG° of n processes. For example, the E° of the A/D pair can be calculated from the Latimer diagram as follows:

$$A \xrightarrow{E^{o}_{A/B}} B \xrightarrow{E^{o}_{B/C}} C \xrightarrow{E^{o}_{C/D}} D$$

$$A + n_{1}e \longrightarrow B \qquad \Delta G^{o}_{A/B} = -n_{1}FE^{o}_{A/B}$$

$$B + n_{2}e \longrightarrow C \qquad \Delta G^{o}_{B/C} = -n_{2}FE^{o}_{B/C}$$

$$C + n_{3}e \longrightarrow D \qquad \Delta G^{o}_{C/D} = -n_{3}FE^{o}_{C/D}$$

$$A + (n_{1} + n_{2} + n_{3})e \longrightarrow D \quad \Delta G^{o}_{A/D} = \Delta G^{o}_{A/B} + \Delta G^{o}_{B/C} + \Delta G^{o}_{C/D} = -(n_{1} + n_{2} + n_{3})F.E^{o}_{A/D}$$

$$=> E^{o}_{A/D} = \frac{n_{1}E^{o}_{A/B} + n_{2}E^{o}_{B/C} + n_{3}E^{o}_{C/D}}{n_{1} + n_{2} + n_{3}}$$

Example: Calculate the potential E° of the reduction of HClO₂ to Cl⁻ in acidic solution.

From the Latimer diagram of chlorine, we can write the half-reactions and reactions that need to determine the standard reduction potential:

$$HClO_{2} + 2H^{+} + 2e \longrightarrow HClO + H_{2}O$$

$$HClO + H^{+} + 1e \longrightarrow \frac{1}{2}Cl_{2} + H_{2}O \qquad E^{o} = + 1.630 V$$

$$\frac{1}{2}Cl_{2} + 1e \longrightarrow Cl^{-} \qquad E^{o} = + 1.358 V$$

$$HClO_{2} + 3H^{+} + 4e \longrightarrow Cl^{-} + 2H_{2}O \qquad E^{o}_{HClO_{2}Cl^{-}} = ?$$

Applying the above calculation we have:

$$E^{0}_{\text{HCIO}_2\text{CI}'} = -\frac{2.E^{0}_{\text{HCIO}_2\text{HCIO}} + E^{0}_{\text{HCIO}_2\text{CI}_2} - + E^{0}_{\text{CI}_2\text{CI}'}}{2 + 1 + 1} = \frac{(2 \times 1.674 + 1.630 + 1.358)}{4} = 1.600 \text{ (V)}$$

2.3. Predict Reaction Products

A new application of the Latimer diagram is to be able to predict reaction products of substances containing elements with several oxidation states. Consider, for example, the reaction of iodide anion with permanganate in acidic solution. The Latimer diagrams of the relevant elements are as follows:



From the diagram above, we see that there are 3 unstable particles with disproportion: HIO, MnO_4^{2-} and Mn^{3+} . In addition, Mn is not stable in acidic environments so there is no need to consider them. Therefore, the diagram is simplified as follows:

$$H_{5}IO_{6} - \frac{+1.70 \text{ V}}{\text{MnO}_{4}} IO_{3}^{-} - \frac{+1.20 \text{ V}}{\text{MnO}_{2}} I_{3}^{-} - \frac{+0.54 \text{ V}}{\text{MnO}_{2}} I_{3}^{-} - \frac{+0.54 \text{ V}}{\text{MnO}_{2}} I_{3}^{-} - I_{3}^{-} I_{$$

If permanganate (MnO_4^-) is added drop by drop to a hydroiodic acid solution HI (excess I), then the reaction product needs to be compatible with the presence of iodide ion. Therefore iodate (IO_3^-) cannot form, because it will react with I- to form I_3^- ion (comproportion). Similarly, MnO_2 does not form because it has the ability to oxidize I. It follows that the total reaction must be:

$$15I^{-} + 2MnO_{4}^{-} + 16H^{+} \longrightarrow 5I_{3}^{-} + 2Mn^{2+} + 8H_{2}O$$

Conversely, if iodide solution is added drop by drop to an acidified permanganate solution (excess MnO_4^-), the reaction product must be consistent with the presence of MnO_4^- . Therefore, Mn^{2+} ion cannot form because it will react with the MnO_4^- ion to produce MnO_2 (comproportion). Then I will not be completely oxidized to the I_3^- ion because the I_3^- ion has the ability to reduce MnO_4^- ion. The fact that the H_5IO_6 - IO_3^- and MnO_4^- - MnO_2 half-reactions are potentially equal (+ 1.70 V) further complicates the problem. Therefore, we see that I⁻ ion is not completely oxidized to IO_3^- or periodic acid (H_5IO_6) but to a mixture of products:

$$I^{-} + 2MnO_{4}^{-} + 2H^{+} \longrightarrow 2MnO_{2} + H_{2}O$$
$$3I^{-} + 8MnO_{4}^{-} + 11H^{+} + 2H_{2}O \longrightarrow 3H_{5}IO_{6} + 8MnO_{2}$$

Note that changing the excess reactants can lead to

different products.

In addition to the Latimer diagram, we also use the Pourbaix (Frost-Ebsworth) diagram to consider the general relationship between oxidation-reduction activity and Bronsted acid-base activity.

The Pourbaix diagram, also known as the E-pH diagram, is a graphical tool used to predict the stability of different oxidation forms of an element in solution. This chart is built based on two main factors:

Oxidation-reduction potential (E°): The ability of an element to attract or lose electrons.

pH: The acidity or basicity level of the solution.

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pH: The acidity or basicity level of the solution.

The Pourbaix diagram can be used to determine the pH and ion concentration conditions required for a particular oxidation form of an element to be stable. This information can then be used to draw a Latimer diagram for that oxidation state. The Pourbaix diagram can also be used to determine the oxidation-reduction reactions that can occur between different oxidation forms of the element. This information can then be used to calculate the oxidation-reduction potentials of those reactions using the Latimer diagram.

3. Conclusion

Using the Latimer diagram will help students easily: (1) Predict the stable oxidation state of the element; (2) Calculate the standard reduction potential of oxidationreduction pairs that are not close to each other; (3) Predict the products of redox reactions. Thereby, you will develop skills such as "prediction", "calculation", "analysis" when using electrode potential values in different environments to conclude oxidation-reduction reactions. This is a difficult content, demonstrating the combination of electrochemical theory and inorganic chemistry to consider oxidation-reduction reactions that occur. Latimer diagram applications will create excitement for chemistry students when studying inorganic chemistry at universities.

Statement of Competing Interests

The Authors have no competing interests.

References

- Atkins, Peter; Overton, Tina. "5. Oxidation and Reduction: The diagrammatic presentation of potential data §5.12 Latimer diagrams". Shriver and Atkins' Inorganic Chemistry. OUP Oxford. 2010, pp. 162–3. ISBN 978-0-19-923617-6.
- [2] Atkins, Peter; Overton, Tina; Rourke, Jonathan; Weller, Mark; Armstrong, Fraser; Hagerman, Michael. *Inorganic Chemistry* (5th ed.). New York: W. H. Freeman. 2010, ISBN 978-1-42-921820-7.
- [3] Atkins, Peter, Jones, Loretta. *Chemical Principles* (3rd ed.), W.H. Freeman and Company. 2005, ISBN 0-7167-5701-X.
- [4] Brown, Susan A.; Brown, Paul L. "The pH-potential diagram for polonium". *The Aqueous Chemistry of Polonium and the Practical Application of its Thermochemistry*. Elsevier.
- [5] Cao Cu Giac, Cao Thi Van Giang and Tran Van Thanh. Designing

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a Learning Project on Thermodynamics for Chemistry Students According to the CDIO Teaching Mode. World Journal of Chemical Education. 2024; 12(1):6-12.

- [6] Cotton, F. Albert; Wilkinson, Geoffrey; Murillo, Carlos A.; Bochmann, Manfred. Advanced Inorganic Chemistry (6th ed.), New York: Wiley-Interscience, 1999, ISBN 0-471-19957-5.
- [7] Greenwood, Norman N.; Earnshaw, Alan. Chemistry of the Elements (2nd ed.). Butterworth-Heinemann. 1997, ISBN 978-0-08-037941-8.
- [8] Henry Freiser. Enhanced Latimer Potential Diagrams Via Spreadsheets. J. Chem. Educ. 1994, 71, 9, 786.
- [9] Lide, David R., ed. CRC Handbook of Chemistry and Physics (87th ed.). Boca Raton, FL: CRC Press. 2006, ISBN 0-8493-0487-3.
- [10] Rieger, P.H. "§1.3 Some Uses of Standard Potentials: Latimer Diagrams". Electrochemistry. Springer. p. 18. 1993, ISBN 978-0-412-04391-8.
- [11] V. Rives-Arnau. Free energy-oxidation state diagrams. Journal of Chemical Education. 1989, 66, 8, 652.
- [12] Vanýsek, Petr. "Electrochemical Series". In Haynes, William M. (ed.). Handbook of Chemistry and Physics (93rd ed.). CRC Press. pp. 5–80. 2012, ISBN 9781439880494.
- [13] W. F. Giauque. "Wendell M. Latimer, Chemist". Science. 1955, 122 (3166): 406–407.
- [14] Zumdahl, Steven S., Zumdahl, Susan A. Chemistry (5th ed.), Houghton Mifflin Company. 2000, ISBN 0-395-98583-8.