

Thermodynamics and Kinetics, Possibility and Actuality

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Abstract A typical kinetic experiment, the persulfate–iodide clock reaction, is selected as an example to illustrate applications of thermodynamic possibility and kinetic actuality in chemical reactions. In the experiment, the strongest reducer, sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$, cannot be directly oxidized by the strongest oxidizer ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and this redox must be realized by an intermediate iodine I_2 [presenting in I_3^- anion, a weaker oxidizer than $(\text{NH}_4)_2\text{S}_2\text{O}_8$]. After I_2 molecules being reduced by $\text{Na}_2\text{S}_2\text{O}_3$ molecules to form I^- ions (a weaker reducer than $\text{S}_2\text{O}_3^{2-}$), the strongest oxidizer begins to oxidize the weaker reducer I^- ions to form I_2 molecules again, which is keeping on the redox circles until the stronger reducer $\text{Na}_2\text{S}_2\text{O}_3$ has been exhausted completely. Why the strongest reducer was not being oxidized by the strongest oxidizer? In this paper we attempt to explain this situation based on the chemical theories of thermodynamics and kinetics.

Keywords: thermodynamics, kinetics, reaction rate, redox reactions

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1. Introduction

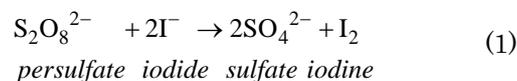
Thermodynamics and kinetics are the basic theories applied in chemical reactions and these theoretical data related to energy and reaction rate can be used to predict whether a reaction will take place. Several factors, including nature of the reaction, concentrations of the reactants, temperature, and the presence of catalysts can influence the observed reaction rate significantly. Chemical reactions must be thermodynamically spontaneous ones. On the contrary, thermodynamically spontaneous reactions may not occur if their reaction rates are very slow, such as the disproportionation of hydrogen peroxide to form oxygen and water, which is a thermodynamically spontaneous one ($E_A^\circ = 1.10\text{V}$, [1] $\Delta G_r^\circ = -zFE_A^\circ = -2 \times 96500(\text{C/mol}) \times 1.10\text{V} = -212.3\text{kJ/mol}$). In fact the commercial hydrogen peroxide with *ac* 30% wt is much stable under ambient conditions. Therefore thermodynamic analysis provides an explanation whether a chemical reaction will take place in view of energy. Kinetic data provide evidence to indicate that if a chemical reaction occurs practically, i.e. at what rate and how much products will be obtained when the reaction is completed or reaches its equilibrium state. Ammonia synthesis is another example. The reaction between gaseous N_2 and H_2 [$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$] is exothermic, thus it should be carried out at low temperature based on the thermodynamic analysis in order to obtain more ammonia. But in practice, this process is carried out at high pressure, high temperature, and in the presence of iron catalysts to reduce the reaction time and achieve higher yield. The optimal performance requires

reaction temperatures around 400°C and pressures from 150-300 atmospheres. [2] Therefore, thermodynamics and kinetics are only essential theories governing chemical reactions.

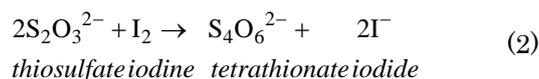
2. Puzzles in a Typically Kinetic Experiment

2.1. The Typical Experiment

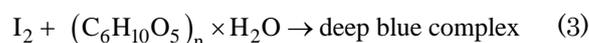
The kinetic experiment is based on a redox reaction to determine its rate equation and activation energy. This redox is described as reaction (1): [3]



In this experiment, the consumption rate of the iodine will be measured to determine its rate equation. As reaction (1) proceeds, the amount of iodine (I_2) produced from it will be reduced by the followed reaction (2):



In order to observe the end point of the reaction easily, starch is added to produce a deep blue starch-iodine complex, which will take place when all thiosulfate is consumed and free iodine forms in solution:



iodine starch

In summary, iodide (I^-) and persulfate ions ($S_2O_8^{2-}$) react to produce iodine (I_2) and sulfate (SO_4^{2-}) in reaction (1). This produced iodine is immediately consumed by the thiosulfate ions [$S_2O_3^{2-}$, reaction (2)]. As soon as all of the $S_2O_3^{2-}$ ions are consumed, the excess iodine produced in the reaction (1) is free to react with starch, turning the solution to blue [reaction (3)]. The added amount of thiosulfate equals to that of the produced iodine in the time taken for the solution to turn to blue.

2.2. Puzzles in the Experiment

In this typical kinetic experiment, a question puzzled us for a long time. According to the redox ability, the involved reagents are listed as below:

Oxidizability: $S_2O_8^{2-} > I_2 > S_2O_3^{2-}$

persulfate iodine thiosulfate

Reducibility: $S_2O_3^{2-} > I^- > S_2O_8^{2-}$

thiosulfate iodine persulfate

This sequence is arranged by the standard electrode potential series (E_A^\ominus , reduction): [1,4]

$E^\ominus(S_2O_8^{2-}/SO_4^{2-}) = 1.96V$

$E^\ominus(Cl_2/Cl^-) = 1.36V$

$E^\ominus(IO_3^-/I_2) = 1.20V$

$E^\ominus(I_2/I^-) = 0.54V$

$E^\ominus(S_4O_6^{2-}/S_2O_3^{2-}) = 0.08V$

Electrode potential is denoted as EMF (electro motive force). EMF of any electrolytic cell is the sum of the EMF produced at two electrodes.

EMF cell = Higher reduction potential - Lower reduction potential.

If the EMF is larger than zero, the cell reaction will proceed spontaneously. On the contrary, if the EMF is smaller than zero, the reverse cell reaction will be more favorable; and If EMF equals to zero, the cell reaction will reach its equilibrium state.

Based on these electrochemical data, as the strongest oxidizer, $S_2O_8^{2-}$ would be able to oxidize Cl^- , $I_2(I^-)$, and $S_2O_3^{2-}$ ($S_4O_6^{2-}$) to form Cl_2 , IO_3^- , and SO_4^{2-} , respectively. But in the kinetic experiment, the strongest oxidant $S_2O_8^{2-}$ only reacts with I^- , which is a weaker reducer than $S_2O_3^{2-}$. Moreover, the oxidized product is I_2 , which does not reach the final oxidative state of IO_3^- .

Why doesn't the strongest oxidizer $S_2O_8^{2-}$ react with the strongest reducer $S_2O_3^{2-}$? Why does the oxidative state stop at I_2 ? Neither books nor articles attempt to explain these questions.

3. Thermodynamic and Kinetic Explanations

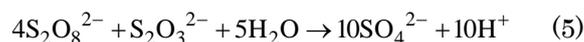
Both thermodynamic theory and kinetic evidence should be employed to explain these puzzles. Therefore the above mentioned reaction processes will be examined by these theories and evidences.

3.1. Thermodynamic Explanation

Before discussing these questions, several reaction must be examined:



persulfate iodine sulfate iodate



persulfate thiosulfate sulfate

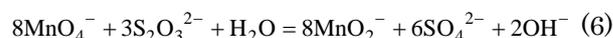
The values of EMF cell and Gibbs free energy changes (ΔG^\ominus) for reactions (1), (2), (4) and (5) are calculated, and the results is as below: [9]

Reaction	EMF cell / V	ΔG^\ominus /kJ·mol ⁻¹
(1)	1.42	-274
(2)	0.46	-89
(4)	0.765	-738
(5)	1.48	-714

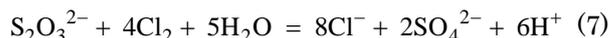
Electrochemical and thermodynamic data indicate that reactions (1), (2), (4) and (5) all belong to spontaneous ones, and they would proceed spontaneously under standard state. Thermodynamic analysis indicates that all above mentioned reactions would take place spontaneously under standard state. But this conclusion is partially contrary to the experimental facts.

3.2. Kinetic Evidences

Several experimental facts are given as below: [1,4]

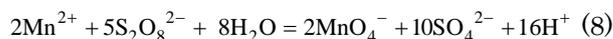


*permanganate manganese oxide
thiosulfate sulfate*



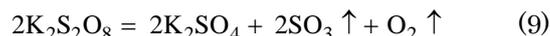
*thiosulfate chlorate
chlorine sulfate*

Over Ag^+ catalyst, Mn^{2+} can be oxidized by $S_2O_8^{2-}$ to produce MnO_4^- in mauve color:



*manganese ion permanganate
persulfate sulfate*

When solid persulfate is heated, it becomes unstable and begins to decompose:



persulfate sulfate sulfur trioxide

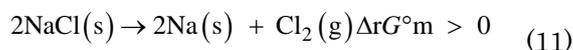
In acid solution, thiosulfate will decompose to form sulfur and sulfur dioxide:



*thiosulfate sulfurous acid sulfur dioxide
sulfur sulfur*

Reactions (6-10) are also spontaneous ones. Four aspects can be refereed in this situation. First, the reactions which can indeed take place must be thermodynamically spontaneous ones. Second, the thermodynamically spontaneous reactions may not take place automatically. Third, several nonspontaneous reactions will take place when pressures, temperature and other conditions have been changed.

i.e.:



sodium chloride sodium chlorine

Reaction (11) is not spontaneous under standard state, but if using electrolytic method, the reaction changes into spontaneous one. Fourth, some nonspontaneous reactions will not occur under any conditions.

Why do not the thermodynamically spontaneous reactions take place?

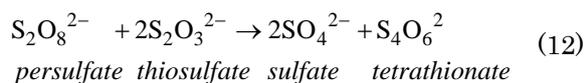
These puzzles can be explained by reaction rate theories. Some reactions, such as the combustion of gasoline in an engine, are explosively fast. Other reactions, such as the rusting of iron, are exceeded slowly. [5] Reaction rates are affected by several factors, including temperature, pressure, concentration, and catalyst. The reaction rate theories, including microcosmic collision theory for calculating rate constants and transition state theory for deciding activation energy, are useful for understanding reaction mechanism. However, those observed reactions must indeed be the ones that are occurring. These kinetic theories need to be used in explanation of the above situations. In the typical kinetic experiment $S_2O_8^{2-}$, $S_2O_3^{2-}$ and I_2 (I_3^-) coexist in the same reaction system, if reactions (4) and (5) took place spontaneously, the final products would be SO_4^{2-} and IO_3^- . In fact, the terminal products are SO_4^{2-} , $S_4O_6^{2-}$ and I_2 (I_3^-) when the reducer $S_2O_3^{2-}$ is exhausted. Therefore reactions (4) and (5) seem as nonspontaneous ones, and they fail to occur under the designed conditions. Research results [6,7] indicate that reactions (4) and (5) indeed carry out under different conditions. Reaction (4) can take place automatically in an alkaline solution; [6] and *thiosulfate* can also be oxidized by *persulfate* slowly to produce *sulfate* and *tetrathionate* with activation energy of 64.8-74.8 kJ·mole⁻¹ [6,7,8]

Although the discussed reactions are all thermodynamically spontaneous, their reaction rates are much different. The reactions in the typically kinetic experiment are arranged according to rate:

$$r_{(2)} > r_{(1)} \gg r_{(4)} \text{ and } r_{(5)}$$

In fact $r_{(4)}$ and $r_{(5)}$ can be ignored, and therefore the reaction rates decide that only the products in middle valence, including *tetrathionate* and *iodine* products, can be obtained in this experiment.

The kinetic reaction can also be described as reaction (12) [reaction (12) = reaction (1) + reaction (2)]:



Reaction (12) cannot occur directly, and it must be initiated by I_2/I^- . Therefore both I_2 and I^- act as catalyst for reaction (12). [6] I^- ions produced by fast reaction (2) are oxidized by $S_2O_8^{2-}$ to form I_2 immediately [reaction (1)]. Reactions (1) and (2) take place alternately, until the reducer $S_2O_3^{2-}$ is exhausted completely, and the accumulated I_2 react with starch to form the deep blue complex, which indicates the termination of the reaction.

4. Conclusions

As a teacher of chemistry and chemical engineering, one should pay more attention to thermodynamic possibility, kinetic actuality and their relationship. Under certain conditions, the reactions with kinetic actuality must be thermodynamically spontaneous ones. Above discussions based on the level of general chemistry or fundamental chemistry is suitable for chemical education in freshmen's chemistry courses. The engrossed research should be based on the level of physical chemistry and its relative experiments. For the freshmen in universities, the concepts of thermodynamic possibility and kinetic actuality must be enhanced and emphasized in guiding their thinking, intellection and ideation during theoretic and experimental educations.

5. Acknowledgements

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