

Analysing the Interaction of Sodium Thiosulfate with Sulfuric Acid

Hasib Sifat,¹ Nikita Platonov,² and Kirill Alatortsev³

¹ Faculty of Physical and Quantum Electronics, ^{2,3} Faculty of Aerophysics and Space Research, ^{1,2,3} Moscow Institute of Physics and Technology, Institutskiy Pereulok, 9, Dolgoprudny, Moscow Oblast, Russian Federation, 141701

Abstract: Back in 1889, Swedish chemist Svante Arrhenius proposed an equation based on the work of Dutch chemist Jacobus Henricus van 't Hoff who had noted in 1884 that the van 't Hoff equation for the temperature dependence of equilibrium constants suggests such a formula for the rates of both forward and reverse reactions. [1] This equation has a vast and important application in determining rate of chemical reactions and for calculation of energy of activation. Arrhenius provided a physical justification and interpretation for the formula. It can be used to model the temperature variation of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions. To see how the reaction rate has changes changing temperature, we did reactions of Sodium Thiosulfate with Sulfuric Acid at two different temperatures and observed the change in concentration with time. In this article, we have shown all the result we got from our experiment and conclude the applicability of the Van't-Hoff rule and the temperature dependence of all the components of Arrhenius Equation. © 2022 The Author(s)

1. Introduction

The oxidative rusting of iron under Earth's atmosphere is a slow reaction that can take many years, but the combustion of cellulose in a fire is a reaction that takes place in fractions of a second. [2] That means the term reaction rate can be defined by the speed at which a chemical reaction takes place and can be determined by measuring the changes in concentration over time. But it affected by a lot of factors, such as the nature of the reactant (ionic, covalent, homogeneous, heterogeneous), physical state of reactant (*gas* > *liquid* > *solid*), surface area of reactant, intensity of light, catalyst, temperature and concentration. Every factor has very important effect on the rate of reaction. Some factors can speed up the reaction depending on what reaction we're doing and some other factors can lower the speed. In our experiment, we independently kept our reactant and product from other factors and made reaction at room temperature first and then at 10°C + room temperature. In most of the reaction, on increasing temperature, rate constant also increases. Van't Hoff rule tells us that the speed of chemical reactions (reaction rate) is doubled, at least, for each 10°C rise in temperature. Using Arrhenius equation we will find the rate constant at two different temperature. Here the most important concept arises which is collision theory, proposed independently by Max Trautz in 1916 [3] and William Lewis in 1918 [4]. It states that when suitable particles of the reactant hit each other with correct orientation, only a certain amount of collisions result in a

perceptible or notable change; these successful changes are called successful collisions. The successful collisions must have enough energy, also known as activation energy, at the moment of impact to break the pre-existing bonds and form all new bonds. This results in the products of the reaction. Increasing the concentration of the reactant brings about more collisions and hence more successful collisions. Increasing the temperature increases the average kinetic energy of the molecules in a solution, increasing the amount of collisions that have enough energy.

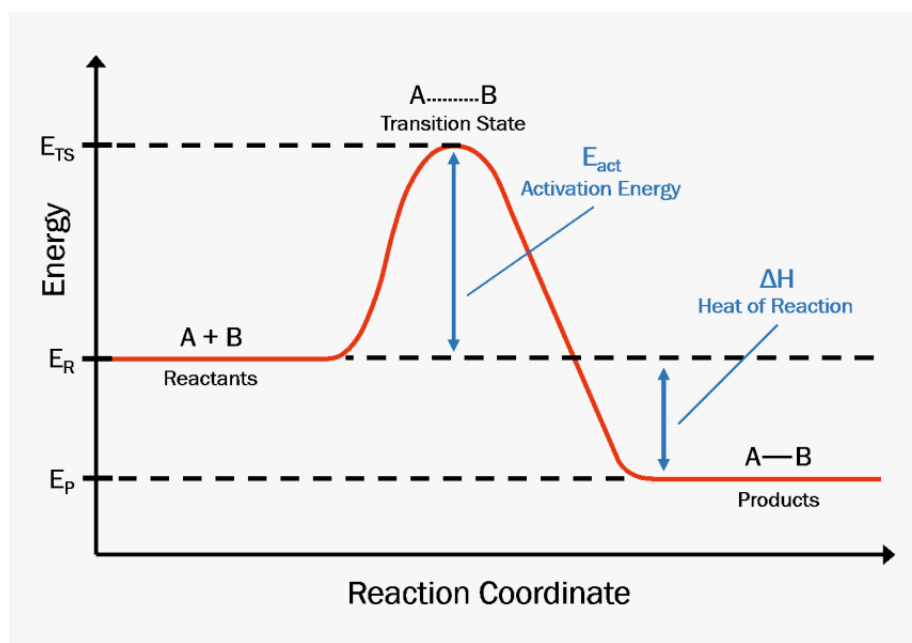


Fig. 1. Reaction Coordinate vs Energy Sample Graph

Now let's discuss a little bit about why the concept of energy arises. All reactions require energy, from the simplest - such as boiling water to turn liquid water into gaseous water - to the complex, such as electrochemical reactions. We can see what is happening to the energy in a reaction using a reaction coordinate diagram. A reaction coordinate diagram is a diagram that plots energy versus reaction progress (Fig. 1). Let's start at 'A+B'. This is the reactants before the reaction has occurred. As the reaction occurs, energy is being added, and this energy is often in the form of heat. So, the line curves up until it reaches a peak (Transition State). After this, the line curves down. In the figure, 'A-B' (the products) is at a lower energy than 'A'. The amount of energy that had to be added is called the activation energy. And the difference in energy is called delta E, which is the difference in energy of the starting materials versus the finished product.

A fraction of molecules which cross the activation energy at temperature T is:

$$e^{-E_a/RT}$$

And we can say,

$$\begin{aligned} \text{rate} &\propto e^{-E_a/RT} \\ k &\propto e^{-E_a/RT} \end{aligned}$$

And we got the Arrhenius equation:

$$k = A.e^{-E_a/RT} \dots\dots\dots(1)$$

Where,

k = rate constant

A = Frequency factor/Arrhenius factor/ pre-exponential factor

e = Exponential constant

E_a = Activation energy

R = Gas constant = 8.314 J/mole/K

T = Temperature

Now, we just simplify the Arrhenius equation for using more conveniently in our calculation later. By taking natural logarithm in both side, we get

$$\begin{aligned} \ln k &= \ln A.e^{-E_a/RT} \\ \ln k &= \ln A + \ln e^{-E_a/RT} \\ \ln k &= \ln A - E_a/RT \ln e \end{aligned}$$

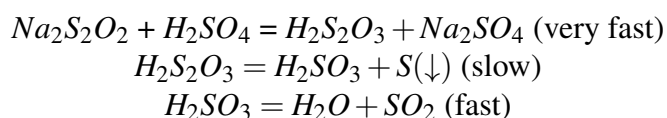
And we get the simplified form of Arrhenius equation:

$$\ln k = \ln A - E_a/RT \dots\dots\dots(2)$$

The order of the reaction we showed in this article, came from a very important concept. It is defined as the dependence of the concentration of all reactants in a chemical reaction on the rate law expression. For example, in a first order chemical reaction, the rate of reaction is entirely dependent on the concentration of one reactant in the reaction. Order of a chemical reaction can be defined as the sum of power of concentration of reactants in the rate law expression is called the order of that chemical reaction. Reactions can be first order reaction, second order reaction, pseudo first order reaction etc. depending on the concentration of the reactants. Order of a reaction is an experimental value. It means it is an experimentally determined parameter. It can have fractional value as well.

2. Experimental Results

The motivation for choosing $Na_2S_2O_2$ and H_2SO_4 is important here. Because it has total three parts of reaction and two of them are so fast that we can't observe them. We just see one part which is the slowest.



In Fig.1, we saw a random graph which is for elementary reaction. Now let's think about the Reaction Coordinate vs Energy Graph for the experiment we did. This type of reaction is call the complex reaction which has more than one step. And for this we will get number of transition state equal to the number of steps of the reaction. The arbitrary figure shows bellow a random visualization of how it look likes.

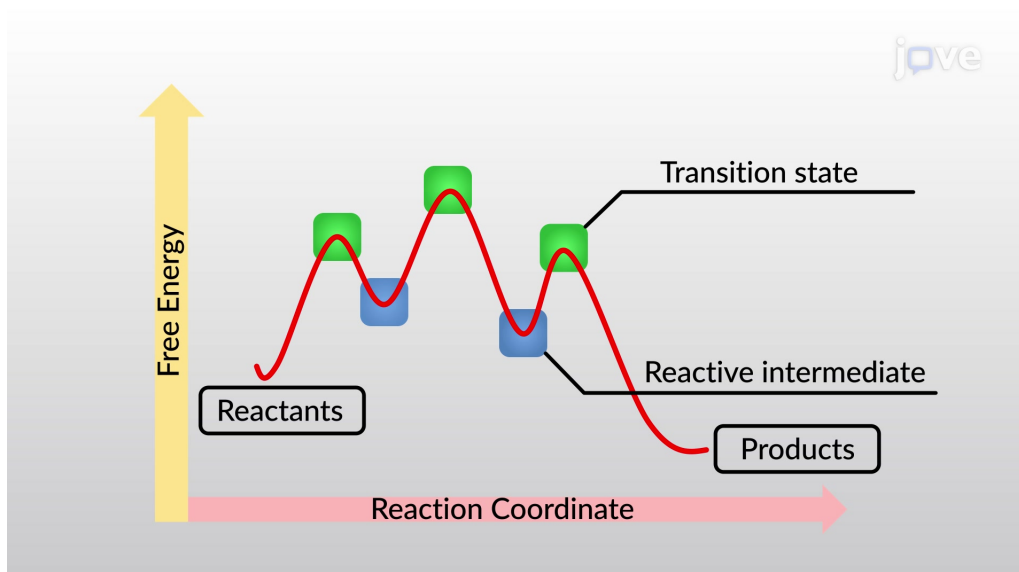


Fig. 2. Reaction Coordinate vs Energy sample graph for complex reaction.

We took $Na_2S_2O_2$, H_2O and H_2SO_4 in test tubes and first made our reaction at $23^\circ C = 296K$ and then at $33^\circ C = 306K$. We used thermostat for increasing the temperature of reactants. As we see from the reaction equation, there will be precipitate of sulfur. We count the required time from the beginning of the reaction to the first trace of sulfur's precipitate. We write down all the data of our experiment.

$Na_2S_2O_2$	H_2O	H_2SO_4
0.5	2	2.5
1	1.5	2.5
1.5	1	2.5
2	0.5	2.5
2.5	-	2.5

Table 1. Volume of reactants

$C_{Na_2S_2O_2}$, mole/L	Time of first precipitate tracing, τ , s	Reaction rate, $1/\tau$, s^{-1}
0.01	129	7.73×10^{-3}
0.02	71	14.08×10^{-3}
0.03	40	25×10^{-3}
0.04	32	31.25×10^{-3}
0.05	24	41.67×10^{-3}

Table 2. Measured quantities for $T_1 = 23^\circ C$

$C_{Na_2S_2O_2}$, mole/L	Time of first precipitate tracing, τ , s	Reaction rate, $1/\tau$, s^{-1}
0.01	94	10.64×10^{-3}
0.02	39	25.64×10^{-3}
0.03	23	43.48×10^{-3}
0.04	16	62.5×10^{-3}
0.05	13	76.92×10^{-3}

Table 3. Measured quantities for $T_2 = 33^\circ C$

3. Results Analysis

After plotting our measured data, we get

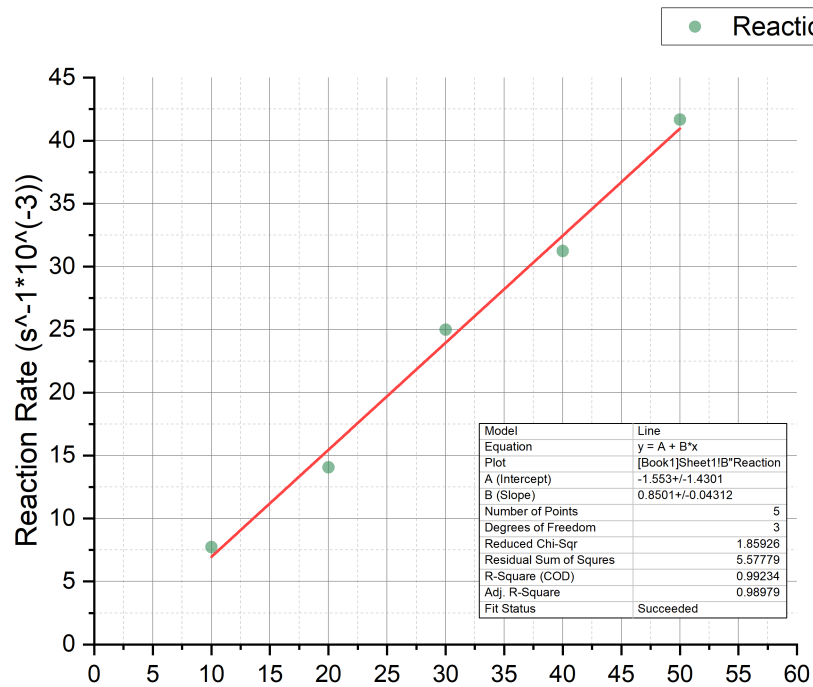


Fig. 3. Dependence reaction rate upon concentration for T_1

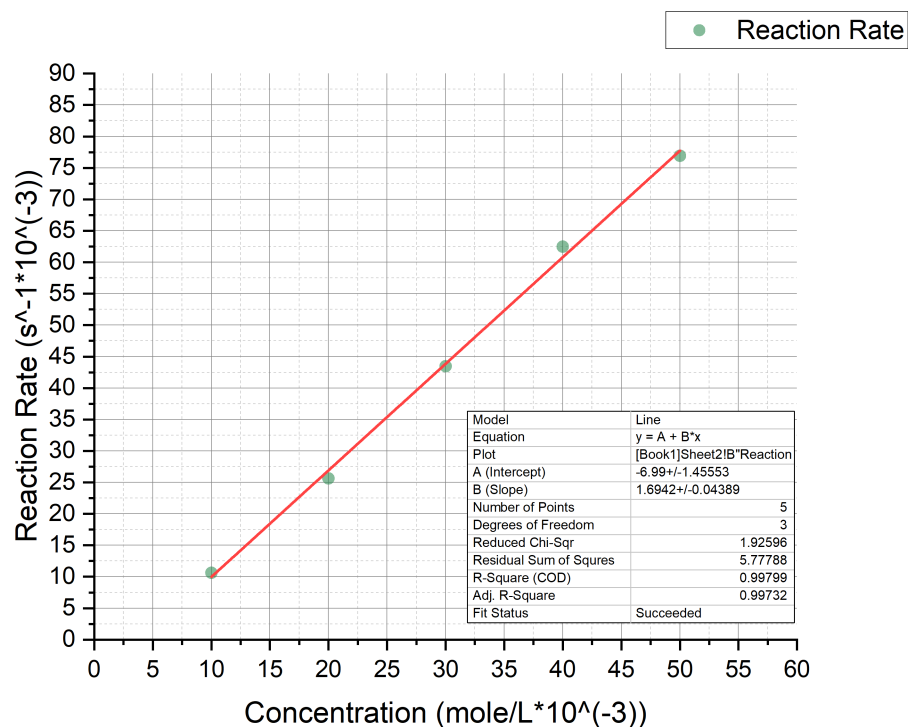


Fig. 4. Dependence reaction rate upon concentration for T_2

The slope of the graph is the value of k_1 and k_2 .

$$k_1 = 0.85 \text{ and } k_2 = 1.69$$

We have two rate constant at two different temperature but the activation energy E_a and frequency factor A are both temperature independent quantity. We get two equation from (2):

$$\ln k_1 = \ln A - E_a/RT_1 \dots \dots \dots (3)$$

$$\ln k_2 = \ln A - E_a/RT_2 \dots \dots \dots (4)$$

From (3) and (4),

$$\begin{aligned} \ln k_2 - \ln k_1 &= \frac{E_a}{RT_1} - \frac{E_a}{RT_2} \\ \ln\left(\frac{k_2}{k_1}\right) &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \dots \dots \dots (5) \end{aligned}$$

From equation(5), the activation energy:

$$E_a = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} = \boxed{51.73 \text{ kJ/mol}}$$

Now, determine the proportion of active collisions by the formula

$$\begin{aligned} \eta_1 &= e^{-E_a/RT_1} = 7.35 \times 10^{-10} \\ \eta_2 &= e^{-E_a/RT_2} = 1.46 \times 10^{-9} \end{aligned}$$

From equation (1), we get,

$$A_1 = \frac{k_1}{e^{-E_a/RT_1}} = 1.15 \times 10^9 \text{ m}^3/\text{mol}/\text{s}$$

$$A_2 = \frac{k_1}{e^{-E_a/RT_2}} = 1.15 \times 10^9 \text{ m}^3/\text{mol}/\text{s}$$

The frequency factor are same for both case.

4. Conclusions

In this paper, we analysed the data that we got from the reaction of $\text{Na}_2\text{S}_2\text{O}_2$ and H_2SO_4 at two different temperature with 10°C interval. As the reaction has total three elementary steps so this type of reaction is called the Complex Reaction and the concept of molecularity of complex reaction isn't defined. As the two steps of the reaction is so fast that we can't observe them. We calculated the reaction rate of the slowest step of the reaction. From our experimental results, we also found the frequency factor is same for both cases. Now if we look at the combination of two previous graphs, we will conclude an important thing.

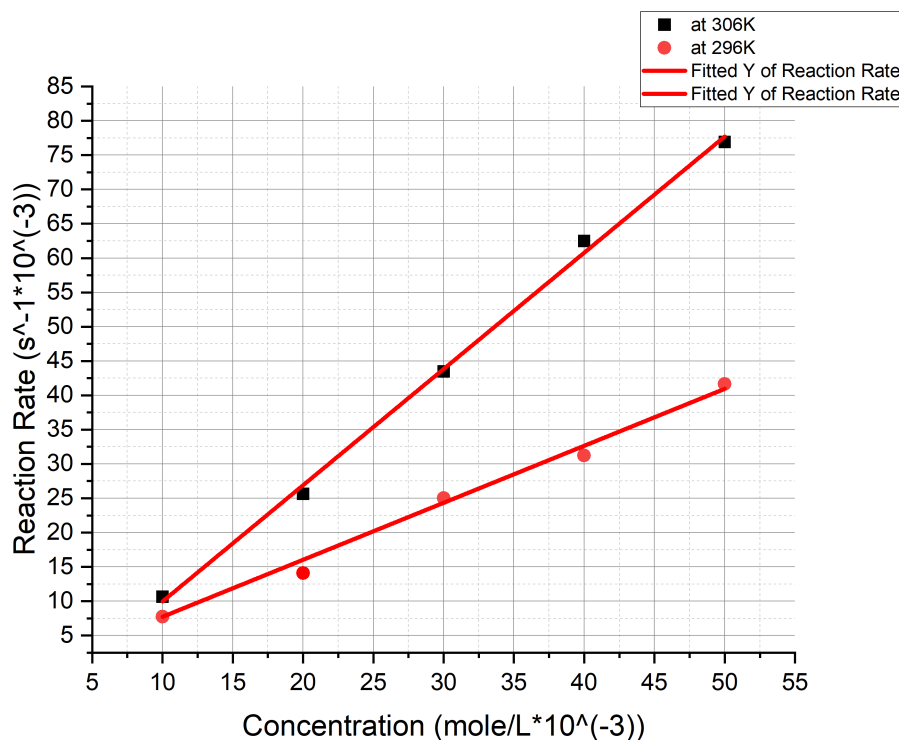


Fig. 5. Comparison of previous two graphs at T_1 and T_2

Here is the actual visualization of the effect of temperature in a reaction rate. We know theoretically that temperature is proportional to reaction rate and from Van't Hoff rule, reaction rate will be doubled by increasing temperature 10°C . So, in our experiment,

$$\frac{k_2}{k_1} = \frac{1.69}{0.85} = 1.988235 \approx 2$$

We conclude that the effect of temperature follows the Van't Hoff rule.

References

1. Wikipedia, https://en.wikipedia.org/wiki/Arrhenius_equation.
2. Wikiwand, https://www.wikiwand.com/en/Reaction_rate.
3. Trautz, Max. <https://onlinelibrary.wiley.com/doi/10.1002/zaac.19160960102> Zeitschrift für anorganische und allgemeine Chemie, Volume 96, Issue 1, Pages 1–28, (1916).
4. IUPAC Compendium of Chemical Terminology(2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "collision theory". [doi:10.1351/goldbook.C01170](https://doi.org/10.1351/goldbook.C01170)).