

## **Stopped-Flow Kinetics**

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## Introduction

Many chemical reactions proceed at a rate difficult to monitor with conventional methods. Often times it is due to the fast rate of the reaction relative to the response time of the machines or to the speed of the mixing of the reagents.<sup>1</sup> Hence, if we were to monitor spectrophotometrically the rate of a fast reaction that has a half-life on the order of milliseconds, we require a spectrophotometer and a computer with a fast time response, as well as an efficient way to mix the reagents and fill the observation cell rapidly. Stopped-flow technique is by far one of the fastest way to fulfill the second requirement. Coupled with modern spectrophotometer and computer, this technique is used to study the kinetics of reactions that reach equilibrium under a second.

In this experiment, using the stopped-flow technique, we studied the kinetics of the reaction between ferric and thiocyanate ions in perchloric acid solution:



where  $k_f$  and  $k_r$  are the rate constants for the forward and reverse reactions. The two reactants are colorless and the product is dark orange. The reagents are stored in two drive syringes. A small volume ( $250\mu\text{L}$ ) of each reagent is expelled into the flow circuit and a same volume is displaced through the mixer to fill the observation cell. Another syringe is connected to the outlet of the cell to collect the solution displaced from the cell – the “waste” from the previous run. The flow is stopped when the “waste” syringe’s plunger hits the mechanical stop. The reaction proceeds in the observation cell and the change in the absorbance of the reaction mixture,

proportional to the amount of product formed, is monitored spectrophotometrically.

This process is repeated three times at each pre-set temperature.

The basic concept used in the kinetics analysis is found in McQuarrie *et al*<sup>1</sup> and Shoemaker *et al*<sup>2</sup>. The detailed analysis pertaining to this particular reaction is given below.

It has been shown that both forward and reverse reactions are first order in their respective reactants<sup>3</sup>, thus we can write the rate law as

$$\frac{d[FeSCN^{2+}]}{dt} = k_f [Fe^{3+}][SCN^{2-}] - k_r [FeSCN^{2+}] \quad (2)$$

When fresh solutions are injected into the observation cell to replace the equilibrated reaction mixture from the previous run, it is as if the original equilibrium is disturbed and needs to be re-established. The process of re-establishing the equilibrium is the reaction between <sup>the</sup> two reactants to form the product. Let

$$[Fe^{3+}] = [Fe^{3+}]_{eq} + \Delta[Fe^{3+}] \quad (3.1)$$

$$[SCN^{2-}] = [SCN^{2-}]_{eq} + \Delta[SCN^{2-}] \quad (3.2)$$

$$[FeSCN^{2+}] = [FeSCN^{2+}]_{eq} + \Delta[FeSCN^{2+}] \quad (3.3)$$

where the subscript "eq" stands for the new equilibrium state. Using the fact that

$$\Delta[Fe^{3+}] = \Delta[SCN^{2-}] = -\Delta[FeSCN^{2+}] \quad (4)$$

we have

$$\begin{aligned} & \frac{d([FeSCN^{2+}]_{eq} + \Delta[FeSCN^{2+}])}{dt} \\ &= k_f ([Fe^{3+}]_{eq} - \Delta[FeSCN^{2+}])([SCN^{2-}]_{eq} - \Delta[FeSCN^{2+}]) \\ & \quad - k_r ([FeSCN^{2+}]_{eq} + \Delta[FeSCN^{2+}]) \end{aligned} \quad (5)$$

Since  $[FeSCN^{2+}]_{eq}$  is a constant, Equation (5) can be simplified to

$$\frac{d(\Delta[FeSCN^{2+}])}{dt} = k_f[Fe^{3+}]_{eq}[SCN^{2-}]_{eq} - k_r[FeSCN^{2+}]_{eq} - \{k_f([Fe^{3+}]_{eq} + [SCN^{2-}]_{eq}) + k_r\}\Delta[FeSCN^{2+}] + O(\Delta[FeSCN^{2+}])^2 \quad (6)$$

Since  $\Delta[FeSCN^{2+}]$  is small, we can ignore the last quadratic term in Equation (6).

Moreover, if we denote the equilibrium constant of the reaction by  $K_{eq}$ , we have

$$K_{eq} = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{2-}]_{eq}} = \frac{k_f}{k_r} \quad (7.1)$$

or 
$$k_r[FeSCN^{2+}]_{eq} = k_f[Fe^{3+}]_{eq}[SCN^{2-}]_{eq} \quad (7.2)$$

Hence the first two terms on the right hand side of Equation (6) cancel and we are

effectively left with

$$\frac{d(\Delta[FeSCN^{2+}])}{dt} = -\{k_f([Fe^{3+}]_{eq} + [SCN^{2-}]_{eq}) + k_r\}\Delta[FeSCN^{2+}] \quad (8)$$

Integrating Equation (8) subject to the condition that  $\Delta[FeSCN^{2+}]_0$  at time  $t = 0$  is equal to  $[FeSCN^{2+}]_{eq}$  gives us

$$\Delta[FeSCN^{2+}] = \Delta[FeSCN^{2+}]_0 e^{-t/\tau} \quad (9)$$

where

$$\tau = \frac{1}{k_f([Fe^{3+}]_{eq} + [SCN^{2-}]_{eq}) + k_r} \quad (10)$$

is the relaxation time, a measure of how long it takes for  $\Delta[FeSCN^{2+}]$  to decay to  $1/e$  of its initial value. Since the starting concentration of thiocyanate is very small, we expect  $[SCN^{2-}]_{eq}$  to be very small and thus negligible.  $Fe^{3+}$  is in great excess, hence  $[Fe^{3+}]$  can be considered constant throughout the reaction. Expressing  $k_r$  in terms of  $K_{eq}$  and  $k_f$ , we can rewrite Equation (10) as

$$\tau = \frac{1}{k_f([\text{Fe}^{3+}] + \frac{1}{K_{eq}})} \quad (11)$$

From Equation (9), we see that a plot of  $\ln \frac{\Delta[\text{FeSCN}^{2+}]}{\Delta[\text{FeSCN}^{2+}]_0}$  versus  $t$  is linear and has a

slope of  $-1/\tau$ . The concentration of the product is directly proportional to its

absorbance at 460nm; therefore  $\frac{\Delta[\text{FeSCN}^{2+}]}{\Delta[\text{FeSCN}^{2+}]_0} = \frac{A_t}{A_\infty}$  and a plot of  $\ln \frac{A_t}{A_\infty}$  versus  $t$

would give us the same straight line with the same slope. Knowing the slope ( $-1/\tau$ ),

$[\text{Fe}^{3+}]$ , and  $K_{eq}$  would enable us to calculate  $k_f$ . The next step is then to find  $K_{eq}$  in

terms of the known  $K_{eq}$ ,<sup>4</sup>  $K_{eq}(298\text{K}) = (146 \pm 5) \text{ M}^{-1}$ , and temperature.

We start with the familiar equations from thermodynamics:

$$K_{eq}(T) = e^{-\frac{\Delta G_{rxn}^o}{RT}} \quad (12)$$

$$\text{and} \quad \Delta G_{rxn}^o = \Delta H_{rxn}^o - T\Delta S_{rxn}^o \quad (13)$$

Plugging Equation (13) into Equation (12), we get

$$K_{eq}(T) = e^{-\frac{\Delta H_{rxn}^o}{RT} + \frac{\Delta S_{rxn}^o}{R}} \quad (14)$$

Knowing the value of  $K_{eq}(298\text{K})$ , we can find the value of  $K_{eq}$  at other temperatures

using

$$K_{eq}(T) = K_{eq}(T_0) e^{\frac{\Delta H_{rxn}^o}{RT_0} - \frac{\Delta H_{rxn}^o}{RT}} \quad (15)$$

where  $T_0 = 298\text{K}$ . We assumed that  $\Delta S_{rxn}^o$  is independent of temperature in this

derivation and the literature value<sup>3</sup> of  $\Delta H_{rxn}^o$  is  $-1600 \text{ cal/mol}$  or  $-6.7 \text{ kJ/mol}$ . Using the

calculated values of  $K_{eq}$  at different temperatures, we are able to calculate the

corresponding  $k_f$ .

Finally we find the activation energy,  $E_a$ , of this reaction using the Arrhenius equation:

$$k_f = Ae^{\frac{-E_a}{RT}} \quad (16)$$

A plot of  $\ln(k_f)$  versus  $1/T$  has a slope of  $-\frac{E_a}{R}$ , from which the activation energy can be easily calculated.

### Experimental

0.020M  $\text{Fe}(\text{NO}_3)_3$  in 0.14M  $\text{NaClO}_4$  and 0.20M  $\text{HClO}_4$ , and 0.0020M  $\text{NaSCN}$  in 0.14M  $\text{NaClO}_4$  and 0.20M  $\text{HClO}_4$  were used as stock solutions. A modified Beckman spectrophotometer was used to monitor the fast change in the absorbance of the reaction mixture at 460nm. The detailed procedure of the experiment can be found in the *Lab Manual*<sup>4</sup>. 15 sets of measurements were obtained between 5°C and 30°C. Data analysis was partially automated by pre-programming the calculation of the relaxation time as part of the data collection software. Relaxation times were obtained by arbitrarily selecting the region of exponential decay and fitting the data with the software.

### Results and Discussion

The temperature and relaxation time of each run are listed in Table I. We realized that it was difficult to obtain highly reproducible relaxation times, as selecting a different fitting range would give a different relaxation time. Thus we arbitrarily decided to fit the data within 30% - 70% of the absorbance change, based on other groups' experience.

Table I. Temperature and relaxation time of the 15 runs.

Run	Temperature (°C)	Temperature (K)	Relaxation time, $\tau$ (s)
1	5.08	279.23	0.813
2	5.08	279.23	0.825
3	5.08	279.23	0.736
4	10.84	284.99	0.242
5	10.87	285.02	0.293
6	10.87	285.02	0.329
7	19.49	293.64	0.144
8	19.51	293.66	0.154
9	19.52	293.67	0.140
10	27.90	302.05	0.055
11	27.89	302.04	0.063
12	27.90	302.05	0.062
13	29.98	304.13	0.054
14	29.99	304.14	0.051
15	29.99	304.14	0.050

We then calculated  $K_{eq}$  and  $k_f$  at these temperatures (Table II) using Equation (14)

and (11).

Table II.  $1/\tau$ ,  $K_{eq}$ , and  $k_f$  for the 15 runs.

Run	$1/\tau$ (s <sup>-1</sup> )	$K_{eq}$ (M <sup>-1</sup> )	$k_f$ (M <sup>-1</sup> s <sup>-1</sup> )
1	1.23	175 ± 6	(5.0 ± 0.4)E+01
2	1.21	175 ± 6	(4.9 ± 0.4)E+01
3	1.36	175 ± 6	(5.5 ± 0.4)E+01
4	4.13	165 ± 6	(1.6 ± 0.1)E+02
5	3.41	165 ± 6	(1.4 ± 0.1)E+02
6	3.04	165 ± 6	(1.2 ± 0.1)E+02
7	6.94	152 ± 5	(2.7 ± 0.2)E+02
8	6.49	152 ± 5	(2.5 ± 0.2)E+02
9	7.14	152 ± 5	(2.8 ± 0.2)E+02
10	18.18	141 ± 5	(7.0 ± 0.7)E+02
11	15.87	141 ± 5	(6.1 ± 0.5)E+02
12	16.13	141 ± 5	(6.2 ± 0.5)E+02
13	18.52	138 ± 5	(7.1 ± 0.6)E+02
14	19.61	138 ± 5	(7.5 ± 0.6)E+02
15	20.00	138 ± 5	(7.6 ± 0.6)E+02

The plot of  $\ln(k_f)$  vs  $1/T$  (Fig. 1) was fitted into a straight line. As each run had a distinct measured temperature, we did not average the  $k_f$  values for each pre-set temperature and instead used all 15 points in our plot. The slope,  $-\frac{E_a}{R}$ , is  $(-8.7 \pm 0.4) \times 10^3 \text{ K}$ .

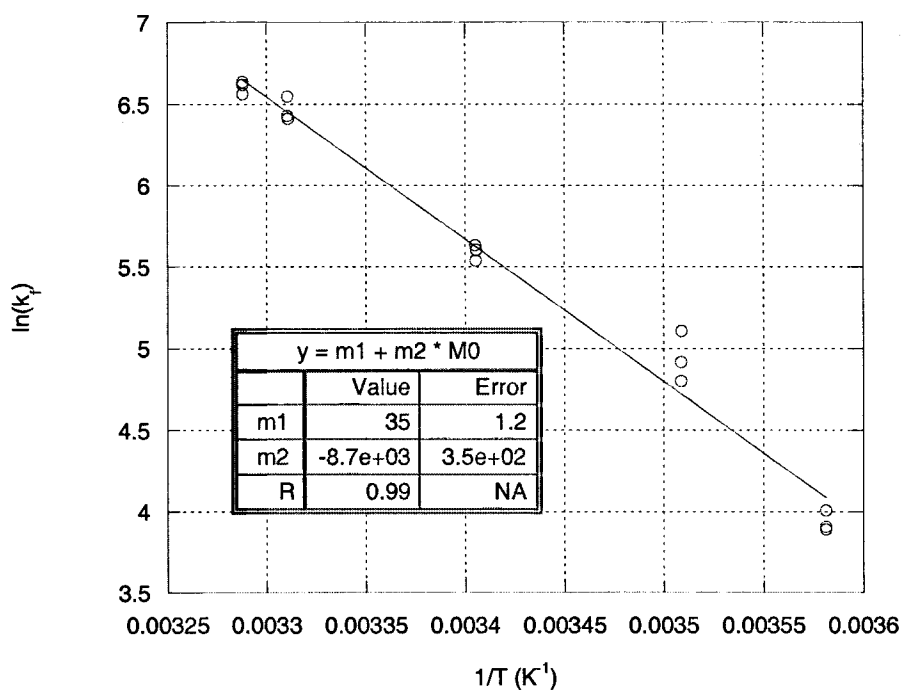


Fig. 1 Plot of  $\ln(k_f)$  vs.  $1/T$ . The slope equals  $-E_a/R$ .

The Arrhenius activation energy,  $E_a$ , was thus found to be  $(72 \pm 3) \text{ kJ/mol}$ .

The error associated with the value of  $E_a$  is probably larger than 3 kJ/mol due to the difficulties encountered in obtaining accurate relaxation times, as mentioned earlier. The error resulted is estimated at 10% of the recorded relaxation time, which would add another 10% error to the final value.



## Summary

Stopped-flow technique was employed in this experiment to measure the rate constant of the forward reaction between ferric and thiocyanate ions at various temperatures. The rate constants were then used to calculate the activation energy of the reaction according to the Arrhenius equation. The activation energy was found to be  $(72 \pm 3)$  kJ/mol.

## References

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- <sup>1</sup> D. A. McQuarrie and J. D. Simon, *Physical Chemistry: A Molecular Approach*, University Science Books, CA, 1997.
  - <sup>2</sup> D. P. Shoemaker, C. W. Garland, J. I. Stienfeld, and J. W. Nibler, *Experiments in Physical Chemistry*, 4th ed., McGraw-Hill Book Co., New York, 1981.
  - <sup>3</sup> J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.* **80**, 2961 (1958).
  - <sup>4</sup> *Chemistry 361 Physical Chemistry: Structure and Dynamics Lab Manual*, Williams College, Williamstown, Fall 2004.