Relaxation Kinetics

THEORY

When a chemical reaction system, in a state of equilibrium, is subjected to a perturbation, it will relax to a new equilibrium position. For kinetic measurements, the perturbation (such as a change in temperature, or pressure, or concentration, etc.) should be accomplished in a time interval which is very small compared to the time scale of the relaxation process. If the new equilibrium position is not far from the initial state, then the kinetics will approximate to first order:

\[
\frac{dx}{dt} = -kx
\]

(1)

where \( x \) is the displacement with respect to the final equilibrium, \( t \) is the time, and \( k \) the rate constant. For example, if the concentration of a reactant (or product) is measured as a function of time, then

\[
x = |C(t) - C(\infty)| > 0
\]

(2)

where \( C(t) \) is the concentration at time \( t \) and \( C(\infty) \) is the concentration at equilibrium.

The relaxation time is defined as \( \tau = 1/k \).

(3)

Integration of equation (1) gives:

\[
\ln x = \ln x_0 - \frac{t}{\tau}
\]

(4)

Here \( x_0 = |C(0) - C(\infty)| > 0 \)

(5)

A plot of \( \ln x \) vs \( t \) gives:

\[
\tau = -1/slope
\]

(6)

In general, provided the perturbation is sufficiently small and fast, any property, \( Y \), of the system which varies with time may be used. The displacement from equilibrium is then given by

\[
x = \left| Y(t) - Y(\infty) \right| > 0
\]

(7)

Temperature jump and relaxation kinetics were used by Eigen and de Maeyer (1955) to measure the forward rate constant of the reaction [M. Eigen and L. de Maeyer (1955) A. Elektrochem. 59, 986]

\[
\text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \quad k_f = 1.4 \times 10^{11} \text{M}^{-1} \text{s}^{-1} \text{ at } 25^\circ\text{C}
\]

Relaxation kinetics following a concentration jump was applied by Swinehart and Castellan (1964) to the slow bichromate-dichromate reaction at 22°C (\( \tau \) of the order of 10 s):

\[
\text{HCrO}_4^- \quad \text{K}_a \quad \leftrightarrow \quad \text{H}^+ + \text{CrO}_4^{2-}
\]

(Rx. 1)

\[
2\text{HCrO}_4^- \quad k_f \quad \leftrightarrow \quad \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

(Rx. 2)

Pertinent equations for this experiment are summarized below:

\[ K_a = f([H^+] [CrO_4^{2-}] [HCrO_4^-]) = 7.4 \times 10^{-7} \text{ M} \quad (8) \]

Dimerization constant: \[ K_d = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} = k_d/\{k_r[H_2O]\} = 50 \text{ M}^{-1} \quad (9) \]

Relaxation time: \[ \frac{1}{\tau} = 4k_f[HCrO_4^-] + k_r[H_2O] \quad (10) \]

Calculate the equilibrium $[HCrO_4^-]$ as a function of the total chromium concentration, the dimerization and dissociation constants, and the pH (or $[H^+]$) (Hint: write down the conservation of mass for chromium and combine this equation with the two equilibrium constants; you will arrive at a quadratic equation in $[HCrO_4^-]$, you should show this equation in your report)

**EXPERIMENTAL PROCEDURE**

Solution A: 0.01 M $K_2Cr_2O_7$ (= 0.02 M in Cr) in 0.1 M $KNO_3$

Solution B: 0.2 M $K_2Cr_2O_7$ (= 0.4 M in Cr) in 0.1 M $KNO_3$

Prepare only 50 ml of solution B in a volumetric flask and the necessary amount of 0.1 M $KNO_3$ (small volumes of sn B can then be transferred to scintillation vials from where is easier to pipet the necessary amounts to prepare sn A). You can use the top loader to weigh $KNO_3$ and $K_2Cr_2O_7$

Place 50 ml of solution A in a beaker equipped with magnetic stirring and adjust to pH 7 with NaOH (solution already prepared by the TA) using a buret. Inject solution B using a syringe while stirring. The pH varies with time as the reaction proceeds.

Repeat last step for at least 5 different volumes of solution B between 0 and 1 ml on a freshly prepared solution of A each time (adjusted to pH 7); and repeat each volume 2 times.

To calibrate the pH meter follow the instructions on the computer desktop or the lab handout. Remember to input the calibration constant and the potential measured at pH=7 in the LabView program. The voltmeter should be on the mV scale, dc mode. Make sure the ground side of the connector from the pH meter goes into the ground of the multimeter.

When the pH meter electrode is not in use, please put in the pH=7 buffer solution!!

**RESULTS**

Your report should include a plot of $\ln x$ vs t (slope = $-1/\tau$) and a plot of $1/\tau$ vs $[HCrO_4^-]$ (slope = 4$k_f$, intercept = $k_r[H_2O]$). Also compute: $K_d = k_f/\{k_r[H_2O]\}$, and answer the following questions:

You will probably note that the computed $K_d$ does not entirely agree with that assumed in Eq. (9) and used to calculate $[HCrO_4^-]$. Does it lie within the estimated error limits? Would it be worthwhile to repeat the calculations with a different $K_d$ or iterating?

What about the variation of $[HCrO_4^-]$ during the run - before equilibrium is reached? Calculate the % change in total Cr concentration for every experiment.

What is the advantage of starting the reaction at pH=7?