## Kinetics: Rate Law Determination Crystal Violet, a.k.a. "Gentian" Visible Spectroscopy

Colors, dyes and textiles have a long history dating back to about 2500 BC, when it is believed that plant and insect dyestuffs were first used in ancient China. Natural sources were used for dyeing until relatively recently when a synthetic dye was accidentally discovered by a young English chemist, William Henry Perkin (1838-1907). Perkin at the age of 18 had set out to synthesize quinine,  $C_{20}H_{21}N_2O_2$ , by oxidizing allyltoluidine  $(C_{10}H_{12}N)$ . However, he had instead accidentally produced the first synthetic dye, aniline purple, more widely known as mauveine. The actual molecular formula of the dye's principal component is  $C_{26}H_{23}N_4^+$ ,  $X^-$ ; X = chloride, sulphate, acetate, etc. It is worth noting that molecular structures of only a few compounds were known with any certainty at that time, and Kekule had only recently recognized the structure of benzene.

Perkin set up a factory on a 6-acre site in West London. At the Royal Exhibition of 1862, Queen Victoria made an appearance in a silk gown, which was dyed with mauveine that was made in the late 1850s. She unveiled a "penny lilac" postage stamp thought to have been dyed with the same compound. Curiously, the "correct" structure for mauveine was only determined in 1994, and a complete stereochemical synthesis of quinine was completed by Gilbert Stork in 2001.

The color mauve fell from fashion in the late 1860s, but Perkin discovered other new dyes. It was said that the water in a canal near his factory turned a different color every week, depending on what dyes were being developed at the time.

In the textile industry, almost 100 liters of water are used to dye a kilogram of fiber. Today, the aqueous effluent from the dyeing processes must be treated, but most local regulations in the United States allow the water to be returned to its natural source (often a local stream or river) without complete removal of all of the chemicals used in the dyeing process.

Many fibers, such as cotton, nylon, and polyesters, absorb large amounts of water. The dyeing process is very energy intensive because the water that is evaporated has an extremely high heat of vaporization. Besides coloring textiles, dyes have been used as acid-base indicators, histological stains for cells, and as fluorophores in immunoassays.

Crystal violet (gentian) is within this class of molecules. It reacts relatively slowly under basic conditions loosing its deep purple color to form colorless solutions. This experiment will determine the rate law and rate constant for the reaction under basic conditions with excess hydroxide ion as the reactant.

Refer to the DVC lab manual pg. 74 and the procedure on pg. 75. Part 3 will not been done. The Beer's Law for part 3 follows.

*Figure 1* shows a beam of light (electromagnetic radiation) before and after it has passed through a solution having a path length, *b*, and a concentration, *c*. The power of the beam is attenuated (diminished) from  $P_0$  to P because of the interactions of the photons and the absorbing particles. Transmittance of the solution is the fraction of light that passes through the solution, P / P<sub>0</sub>. In infrared spectroscopy it is often plotted as percent transmission versus frequency (cm<sup>-1</sup>).

Absorbance (A) is expressed as a logarithmic function where the absorbance of a solution increases exponentially as attenuation of the beam becomes larger (less transmittance). Absorbance is directly proportional to the path length, b, through the solution and the concentration, c, of the absorbing species shown in the equation: A = abc, where a is a proportionality constant called *absorptivity*. If the concentration is expressed in molarity (M) and the cell length in centimeters, the absorptivity is called

the *molar absorptivity* and given the symbol,  $\mathcal{E}$ . It has also been referred to as the *molar extinction coefficient*.





Figure 1

Beer's Law will be used to quantitatively determine the respective concentrations of crystal violet from measured absorbances at different times during the reaction of Crystal Violet with hydroxide ion. This data will be plotted against time and processed as instructed on pp. 77-78. Complete items #10 and 16-20.

Results/ Conclusions are to include: the integrated rate law for each run using the pseudo rate constant, the overall rate law and rate constant, the order of each reactant, the overall order of reaction, and the  $\frac{1}{2}$  life for the reaction.

## **Beer's Law Plot:**

Crystal Violet (Gentian Violet):



*Note:* The standard curve is for a neutral solution,  $pH \approx 7$ .