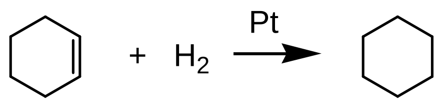
Chemistry 4011/8011 Monday, October 2

Section Question 4

The hydrogenation of pure cyclohexene over solid platinum shows pseudo-half-order kinetics with respect to hydrogen.



$$\frac{-\partial[H_2]}{\partial t} = k_{obs}[H_2]^{1/2}, \quad k_{obs} = k[\text{cyclohexene}]$$

(The expression above is an *overall* rate law for the reaction; there is no way to get an exponent of ½ from an elementary rate law.)

a) Using the simplified, pseudo-half-order expression above (i.e., assuming constant cyclohexene concentration over the entirety of the reaction), write an integrated rate law that expresses the concentration $[H_2]_t$ as a function of time.

b) The half-life $t_{½}$ for this process depends upon both the rate constant k_{obs} and the initial solution concentration $[H_2]_0$. Write an equation that describes $t_{½}$ in terms of these variables (and has the form "$t_{½}$ = ...").

c) A 1 L pressure (Parr) vessel, fitted with a pressure gauge, was filled to the top with solid Pt shavings and liquid cyclohexene and tared on a balance. Next, 0.02 g H_2 was added under pressure (as measured by the balance), and the vessel sealed and shaken to make the hydrogenation proceed. Although there was no way to monitor the concentration of dissolved hydrogen directly over time, the pressure in the small headspace above the liquid was monitored, and this was used to evaluate the total *fraction* of consumed hydrogen (by Henry's Law). After 65 minutes, the gas pressure in the vessel had fallen by half. What is the fundamental rate constant k (not k_{obs}) for this reaction?