

CHEM 3410: Physical Chemistry I — Fall 2008

November 12, 2008

Lecture 30: Determining rate laws

### References

1. Levine, *Physical Chemistry*, Sections 16.1–4

### Key Concepts

- By using integrated rate laws, we can identify reactions of 0th, 1st, and 2nd order. We can also find expressions for the half life, which is the time it takes for the initial concentration to decrease to half its original value.
- For first order kinetics:

$$\text{rate} = k[A] = -\frac{d[A]}{dt}$$

(Note: the coefficient of  $\frac{1}{a}$  is folded into the constant  $k$ )

The integrated rate law would be:

$$\ln[A] = \ln[A_o] - kt$$

This expression is the integrated rate law for 1st order kinetics. If we plot  $\ln[A]$  vs  $t$  and obtain a straight line, we can say with reasonable confidence that the reaction is 1st with respect to  $[A]$ . The slope of the line is equal to  $-k$ . We have to be careful and check other kinetics (0th and 2nd order) as well. The half life for first order kinetics is:

$$t_{1/2} = \frac{\ln 2}{k}$$

- For second order kinetics:

$$\text{rate} = k[A]^2 = -\frac{d[A]}{dt}$$

Integrating, we obtain the integrated rate law for second order kinetics:

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

To determine if the kinetics are second order, we can plot  $\frac{1}{[A]}$  v  $t$ . If the plot is a straight line, the slope will be the rate constant. The half life for this case would be:

$$t_{1/2} = \frac{1}{k[A]_o}$$

- For zeroth order kinetics:

$$\text{rate} = k[A]^0 = k$$

The integrated rate law is:

$$[A] = [A]_o - kT$$

which would be a straight line when  $[A]$  is plotted versus  $t$ . The half life for this case would be

$$t_{1/2} = \frac{[A]_o}{k}$$