April 12, 2002

# CH 342 S02, Homework 9

due Monday, April 13, 2002

This assignment will be covered in class. No late assignments will be accepted.

## Chemical Reaction Kinetics

The following problem draws on information in 25.2.

1. The initial rate of consumption of A $r_o$ = -d[A]$_o$/dt by a chemical reaction A + 2B $\rightarrow$ products is measured as a function of initial concentrations of four components A, B, C, and D. Results are tabulated below. Determine the values of the reaction orders for the empirical rate expression $r_o$ = $[A]^\alpha[B]^\beta[C]^\gamma[D]^\delta$. Assume the reaction orders can be values in increments of $\pm$ 1/2 only.

| | Initial Concentration [mol/L] | | | |
|---|---|---|---|---|
| Initial Consumption Rate [mol/L s] | A | B | C | D |
| 1.00 | 1.00 | 1.00 | 0.010 | 0.010 |
| 2.05 | 2.00 | 1.00 | 0.010 | 0.010 |
| 5.62 | 2.00 | 2.00 | 0.010 | 0.010 |
| 0.21 | 1.00 | 1.00 | 0.050 | 0.010 |
| 1.01 | 1.00 | 1.00 | 0.010 | 0.050 |

The following problems draw on information in 25.3.

2. A certain reaction is found to be first order in [A] with a rate constant of 4.5 $\times 10^{-5}$ $s^{-1}$.

   a) Starting from $[A]_o$ = 1.00 mol/L, how long is required (in s) for [A] to drop to 0.75 mol/L? Use the equation that relates concentration and time for a first order reaction.

   b) Starting from $[A]_o$ = 1.00 mol/L, how long is required (in s) for [A] to drop to half of its initial value? Use the equation for half-life for a first order reaction.

   Extra Credit: Consider a first order reaction in [A]. The time for concentration to decrease from an initial value $[A]_o$ to a value $f[A]_o$ can be expressed as $t = -\ln(f)\, t_{1/2}/\ln(2)$, where $t_{1/2}$ is the half-life of the reaction. Derive (prove) the above expression.

   Extra Credit: **Chemistry in Today's World:** Carbon 14 dating relies on the first order decay (removal) of $^{14}C$ after a living organism dies while the amount of $^{12}C$ stays constant. The first order half-life of $^{14}C$ is 5,700 yrs. Analysis of a skeleton found in the UAH parking lot determines that it has a $^{14}C$ concentration that is 40% of the value in living organisms today. How long ago did the animal die?

3. A certain reaction is found to be second order in [A] with a rate constant of 4.5 $\times 10^{-5}$ mol/L s.

a) Starting from $[A]_o$ = 1.00 mol/L, how long is required (in s) for [A] to drop to 0.75 mol/L? Use the equation that relates concentration and time for a second order reaction.

b) Starting from $[A]_o$ = 1.00 mol/L, how long is required (in s) for [A] to drop to half of its initial value? Use the equation for half-life for a second order reaction.

Extra Credit: Consider a reaction that is second order in [A]. Prove the following:

$$t_{(1/2)^n} = \frac{\sum 2^{n-1}}{k[\mathrm{A}]_o}$$

In the above formula, $n$ is the number of periods that concentration will be cut successively in half. For example, when $n = 3$, concentration will be cut by a factor of 1/8 of its initial value $[A]_o$ in a period of $7/k[A]_o$.

The following problem draws on information in 25.4.

4. The first order rate constant for a reaction A $\rightarrow$ B is 2.5 $\times 10^{-7}$ s$^{-}$1. The equilibrium constant for the reaction is 0.45. What is the first order rate constant for the reaction B $\rightarrow$ A? Use the relationship between forward and reverse rate constants and equilibrium constant.

The following problems draw on information in 25.5.

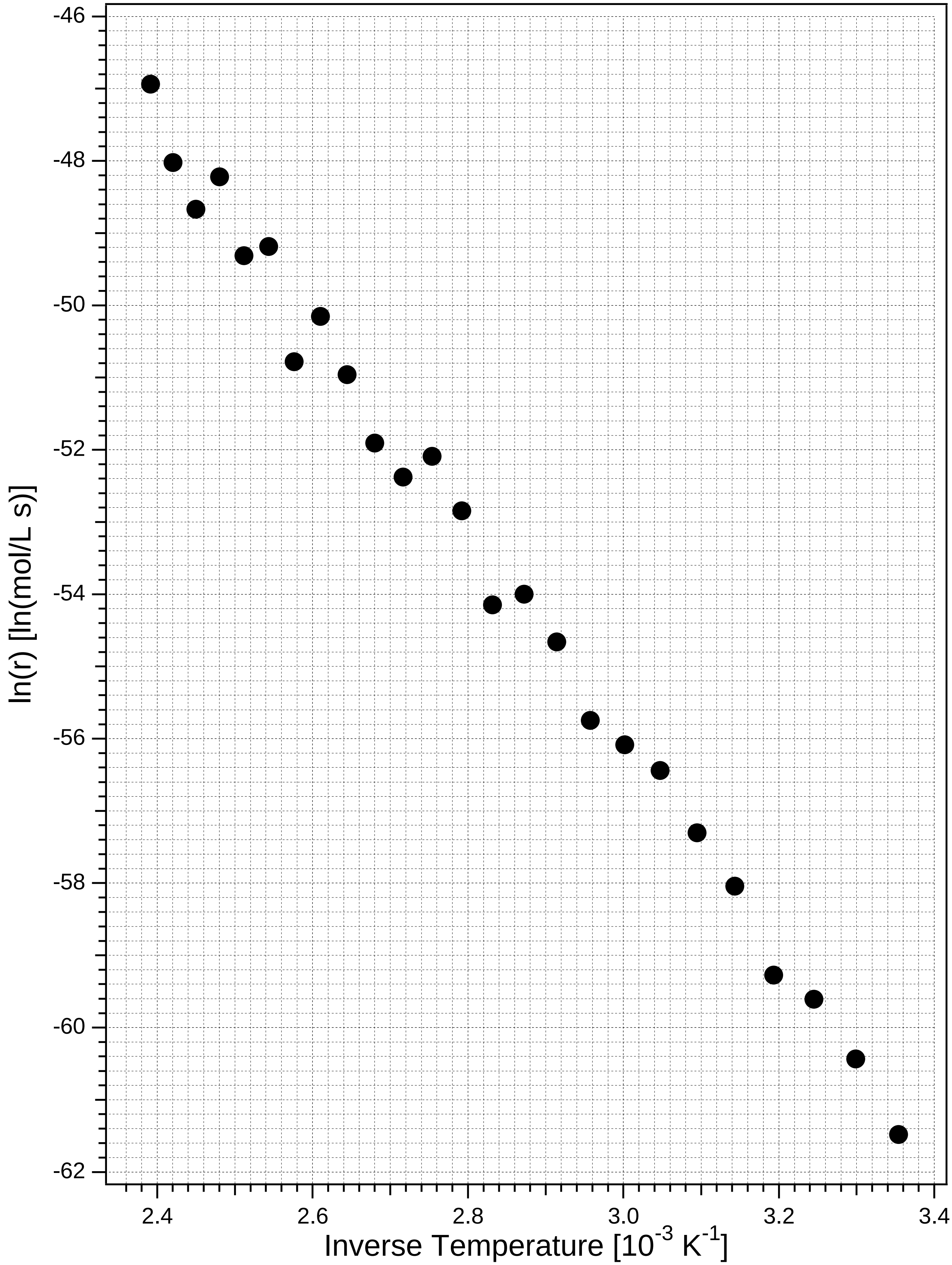
5. A plot of $\ln(r)$ versus inverse temperature is attached at the end of this assignment. Determine the activation energy and pre-exponential for the chemical reaction. Activation energy $E_{act}$ is determined from slope $m$ as $m = -E_{act}/R$. Pre-exponential $ko$ is determined from intercept $b$ as $b = \ln(ko)$.

   Extra Credit: Determine the uncertainty in activation energy from the data plot.

6. A certain reaction has an overall rate constant $k = k_1 + k_2$ where $k_1 = ko_1 \exp(-E_1/RT)$ and $k_2 = ko_2 \exp(-E_2/RT)$. Prove the true activation energy for the reaction has the overall form

$$E_{act} = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

   Overall activation energy is determined from the equation $E_{act} = R\,\frac{d\ln(r)}{d(1/T)}$.



-46
-48
-50
-52
-54
-56
-58
-60
-62
ln(r) [ln(mol/L s)]
2.4
2.6
2.8
3.0
3.2
3.4
Inverse Temperature [10-3 K-1]