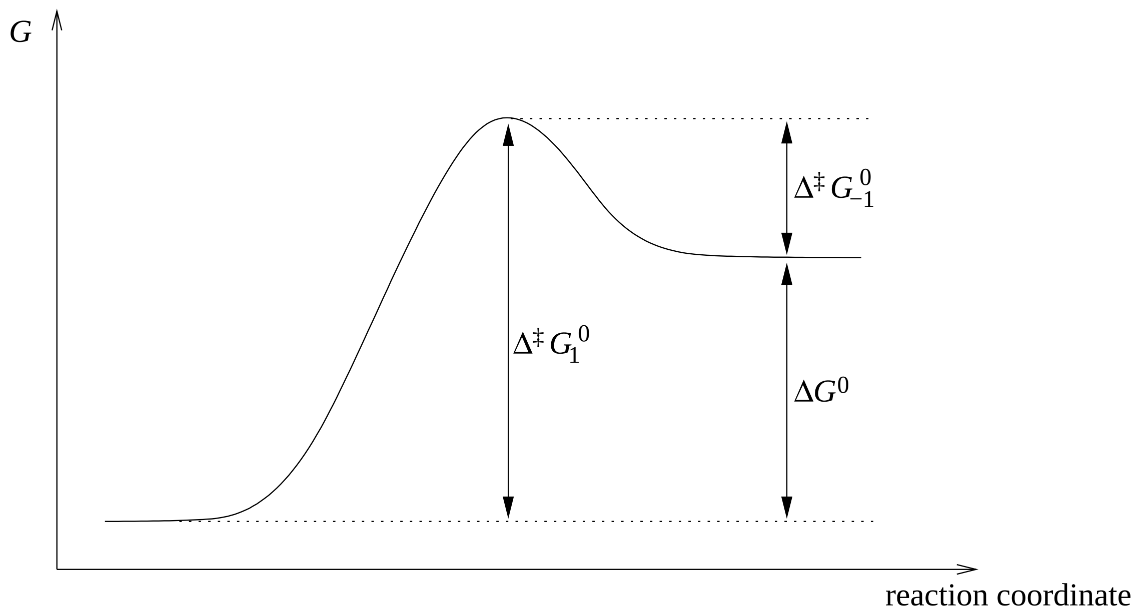
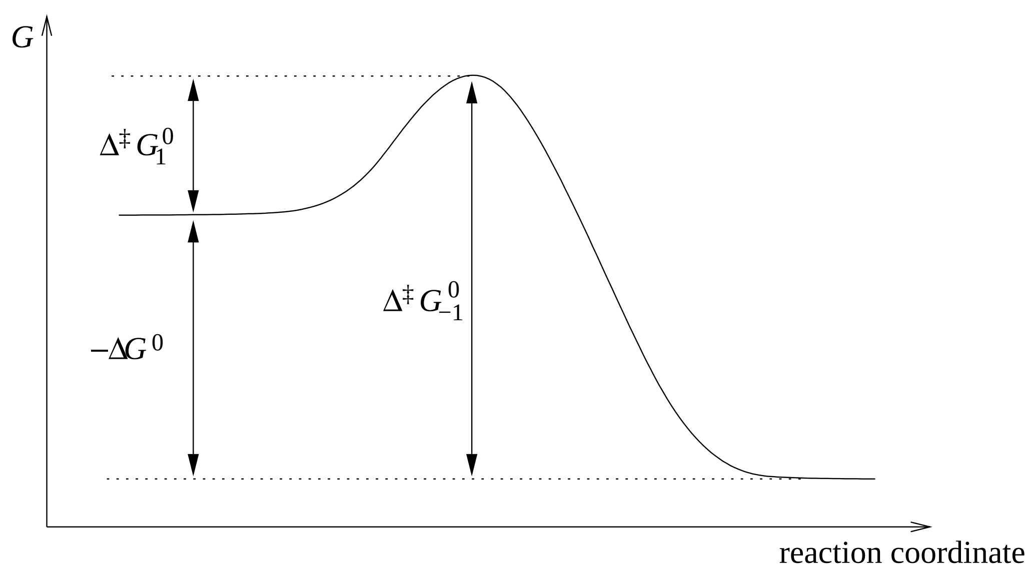
Chemistry 2850 Test 3 Solutions

1. Here is my diagram for an endoergic reaction:



For an exoergic reaction, we would have



In either case, we can read off the following relationship from the diagram:

$$\Delta G^{\circ} = \Delta^{\ddagger}G_1^{\circ} - \Delta^{\ddagger}G_{-1}^{\circ}.$$

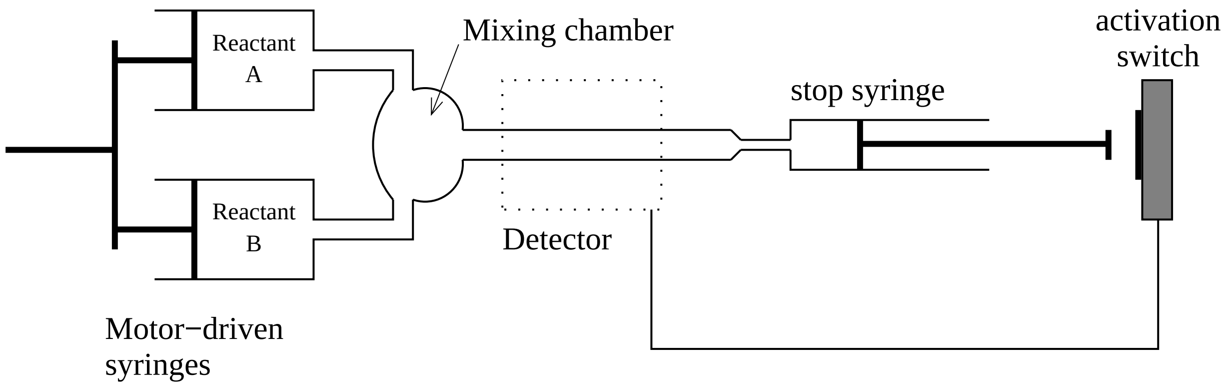


Figure 1: Diagram of a stopped-flow apparatus

2. (a) This is a radical recombination reaction for which the activation energy should be zero. The diameter of an H atom would be twice the radius, or 74 pm. The collision theory preexponential factor, which should equal the rate constant, would be

$$\begin{aligned} k = A &= 2Ld^2\sqrt{\frac{\pi RT}{M}} \\ &= 2(6.022\,142\,0 \times 10^{23}\,\mathrm{mol}^{-1})(74 \times 10^{-12}\,\mathrm{m})^2 \\ &\quad \times \sqrt{\frac{\pi(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{1.007\,94 \times 10^{-3}\,\mathrm{kg/mol}}} \\ &= 1.83 \times 10^7\,\mathrm{m^3mol^{-1}s^{-1}}. \end{aligned}$$

(b) The rate constant is inversely proportional to the square root of the molar mass. Thus the rate constant for the D + D reaction should be smaller by a factor of the square root of 2.

3. Figure 1 shows a diagram of the main parts of a typical stopped-flow apparatus. Two motor-driven syringes deliver the reactants to a mixing chamber. After leaving this chamber, the reactive mixture enters a cuvette which, as it fills, pushes out a stop syringe. The stop syringe eventually hits a switch which both stops the motor and starts the detection system.

The stopped-flow method was designed to address two common problems which come up in studying reactions:

(a) Many reactions are too fast for “pipette-and-stir” methods. Everything about the stopped-flow experiment is designed for speed: The motor-driven syringes can deliver reactants rapidly to the mixing chamber, which in turn is designed to rapidly and efficiently mix the reactants. The apparatus is fairly small in scale, so the cuvette can be filled rapidly. Finally, the use of electronics to control the syringes and data-acquisition system also allow for very fast measurements.

(b) In a stopped-flow system, we only need to fill the small volume which includes the mixing chamber, cuvette and stop syringe. Thus, only very small volumes of solution are required, which is convenient when the reactants are either expensive or hard to make in large quantities.

4. (a) Experiments 1 and 2 are replicates. Comparing experiment 1 to 3, we have a ratio of $[H^+]$ of $0.26/0.062 = 4.2$, and a ratio of rates of $5.4/1.1 = 4.9$. Comparing experiments 2 and 3, we get the same ratio of H^+ concentrations, and a ratio of rates of $5.4/1.3 = 4.2$. Both comparisons are roughly compatible with a first-order dependence of the rate on the hydrogen ion concentration.

Comparing experiments 5 and 6, we have a ratio of HCOOH concentrations of $0.66/0.16 = 4.1$, and a ratio of rates of $1.2/0.28 = 4.3$. Comparing experiments 6 and 7, we have a ratio of [HCOOH] of $1.6/0.66 = 2.4$ and a ratio of rates of $2.7/1.2 = 2.3$. These data suggest a first-order relationship in [HCOOH] also.

The rate law is therefore

$$v = k[H^+][HCOOH].$$

Assuming this rate law, we can calculate k for each experiment:

Experiment	$k/10^{-4}\text{kg mol}^{-1}\text{s}^{-1}$
1	1.8
2	2.1
3	2.1
4	1.8
5	1.8
6	1.7

We average these six measurements to get

$$k = 1.9 \times 10^{-4}\,\text{kg mol}^{-1}\text{s}^{-1}.$$

(b) We just need the slope and intercept of the graph of $\ln k$ vs $1/T$:[1]

$T^{-1}/10^{-3}\text{K}^{-1}$	2.257	2.070	1.949	1.808
$\ln(k/\text{kg mol}^{-1}\text{s}^{-1})$	-11.107	-7.581	-5.599	-2.765

My graph is shown in Fig. 2. The slope and intercept are

$$\begin{aligned}
\text{slope} &= -18\,425\,\text{K} \\
\text{intercept} &= 30.47 \\
\therefore E &= -R(\text{slope}) \\
&= -(8.314\,472\,\text{J K}^{-1}\text{mol}^{-1})(-18\,425\,\text{K}) \\
&= 153\,\text{kJ/mol}
\end{aligned}$$

[1] An ambitious student might have added the fifth point calculated in part a of this question.

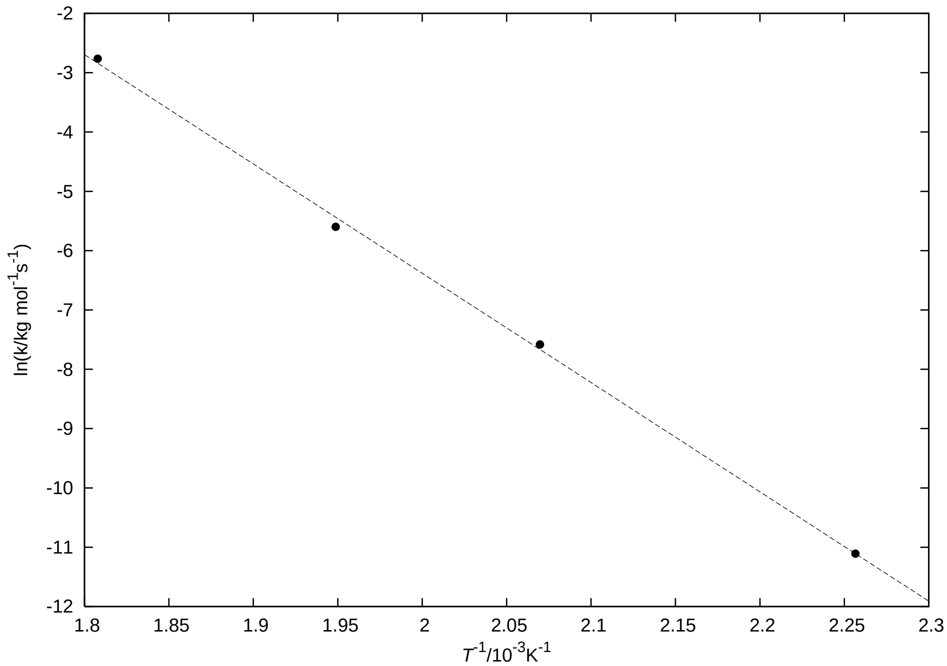


Figure 2: Arrhenius plot for problem 4b.

$$\begin{aligned} \text{and} \quad A &= e^{\text{intercept}} = e^{30.47} \\ &= 1.7 \times 10^{13}\,\text{kg}\,\text{mol}^{-1}\text{s}^{-1} \end{aligned}$$