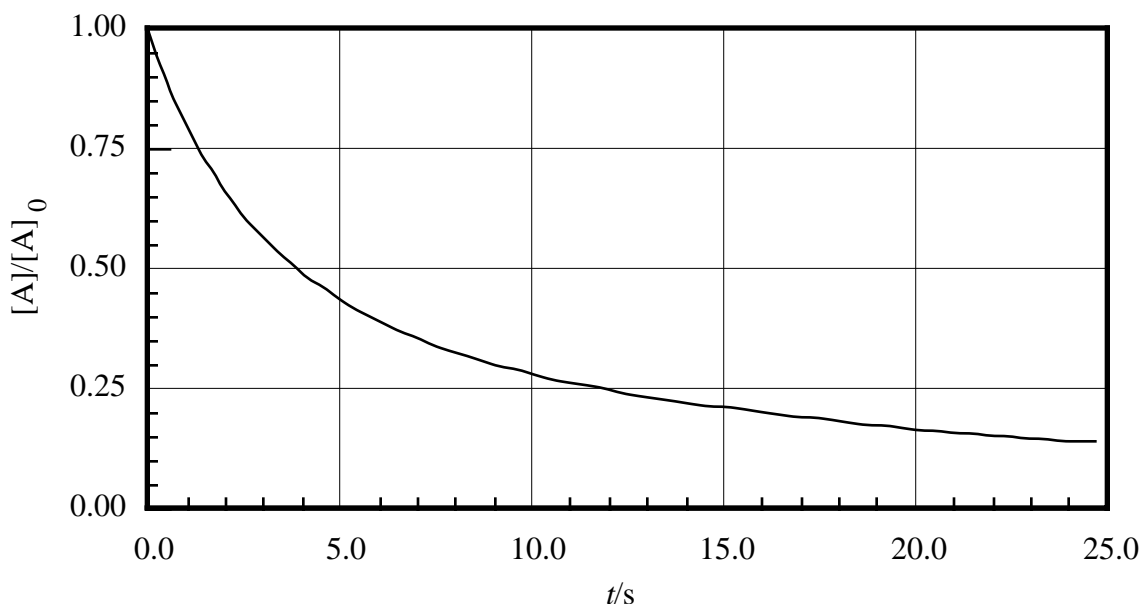


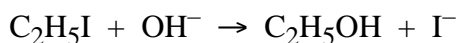
Practice Chem 6 Exam 1

These problems are from exams given in 1993 and 1994. Each exam contained a page of universal constant values and common equations; yours will, too!

1. The graph below shows the relative amount of a reactant A as it disappears in time in an experiment begun with $[A]_0 = 2.5 \times 10^{-3}$ M.



- (a) The net reaction here is simply $2A \rightarrow B$. Use the graph to deduce the net reaction **rate law** and **rate constant**. Explain briefly how you arrived at your answer
- (b) What is the **rate of production of B** (i.e., $d[B]/dt$) at $t = 10.0$ s?
2. The experimental rate constant for the reaction



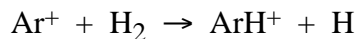
when run in a pure ethanol solvent is:

$$k_{\text{exp}} = 0.368 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \quad \text{at } T = 305.17 \text{ K}$$

$$k_{\text{exp}} = 6.71 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \quad \text{at } T = 332.90 \text{ K}$$

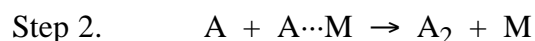
and the rate law is $\text{Rate} = k_{\text{exp}}[\text{C}_2\text{H}_5\text{I}][\text{OH}^-]$. In a new experiment, this reaction is run at **320 K** with initial concentrations $[\text{C}_2\text{H}_5\text{I}]_0 = 0.25 \text{ M}$ and $[\text{OH}^-]_0 = 10^{-4} \text{ M}$. Calculate the time required for the OH^- concentration to fall to half its initial value. **Note:** The temperature is **320 K**, $[\text{C}_2\text{H}_5\text{I}]_0 \gg [\text{OH}^-]_0$, and you can neglect the reverse reaction. Start by finding the rate constant at 320 K.

3. At 300 K, the rate constant for the elementary reaction



is $6.6 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This reaction has been extensively studied in electric discharges through Ar/H₂ gas mixtures, and it is found experimentally that the reaction has **zero** activation energy. At 300 K, the relative speed of Ar⁺-H₂ collisions is 1820 m s⁻¹. Use the collision model's expression for the rate constant, assume the steric factor is 1, and tell me how far apart the Ar⁺ and H₂ are when they react. Express your answer in Å units where 1 Å = 10⁻¹⁰ m.

4. We discussed in class that the net reaction $\text{A} + \text{A} \rightarrow \text{A}_2$ can't happen without a third body entering the collision. Sometimes, this third body doesn't actually strike the two A molecules at the same time they are striking each other. In a mechanism known as the *chaperone* mechanism, the third body (call it M) collides with one A molecule in such a way that the two linger in each other's vicinity for a reasonable time, forming a loosely bound species we represent as A...M. In a second step, the second A molecule collides with A...M to form the stable A₂ product, releasing M. We write this mechanism as



Let k_1 represent the rate constant for step 1 in the forward direction, k_{-1} represent its reverse rate constant, and k_2 represent that for the second step. Use the steady-state approximation to find the rate of the net reaction (expressed as $d[\text{A}_2]/dt$) in terms of these rate constants, [A], and [M]. The usual experimental situation has $[\text{M}] \gg [\text{A}]$ so that $k_{-1} \gg k_2[\text{A}]$. How does your general expression simplify under these conditions?

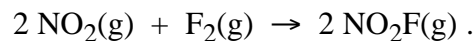
5. The $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ reaction in the gas phase has had a long history. In 1941, two chemists, Taylor and Crist, measured rate constants for this reaction at two temperatures and in both directions. They found:

forward rate constant: $k_f = 67.0 \text{ M}^{-1} \text{ s}^{-1}$ at 698.6 K, $15.6 \text{ M}^{-1} \text{ s}^{-1}$ at 666.8 K

reverse rate constant: $k_r = 1.24 \text{ M}^{-1} \text{ s}^{-1}$ at 698.6 K, $0.259 \text{ M}^{-1} \text{ s}^{-1}$ at 666.8 K

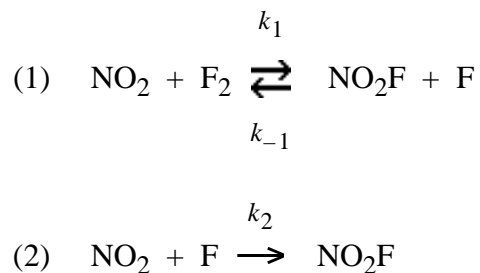
- (a) What is the **activation energy in the forward direction** for this reaction?
- (b) What is the **equilibrium constant at 666.8 K**?
- (c) Sketch a graph of the energy change along the reaction coordinate during this reaction given that the activation energy in the **reverse direction** is 191 kJ mol⁻¹.

6. Consider the net reaction



(a) Write an expression for the rate of this reaction in terms of **time derivatives of each reactant and product**.

(b) Now consider the following plausible two-step reaction mechanism for this net reaction:



Write an expression for the **time derivative of the intermediate's concentration in this mechanism**.

(c) Write the **net reaction rate law** assuming this mechanism is correct and **assuming k_2 is by far the smallest rate constant**.

(d) Experimentally, it is found that under the initial conditions $[\text{F}_2] \gg [\text{NO}_2]$, doubling the initial concentration of NO_2 doubles the initial rate. Does this agree with your rate law's predictions from part (c) above? If it does, tell me why you think so. If it does not, tell me why not. If the experiment is ambiguous (i.e., it neither confirms nor refutes any part of your rate law), explain that, too.