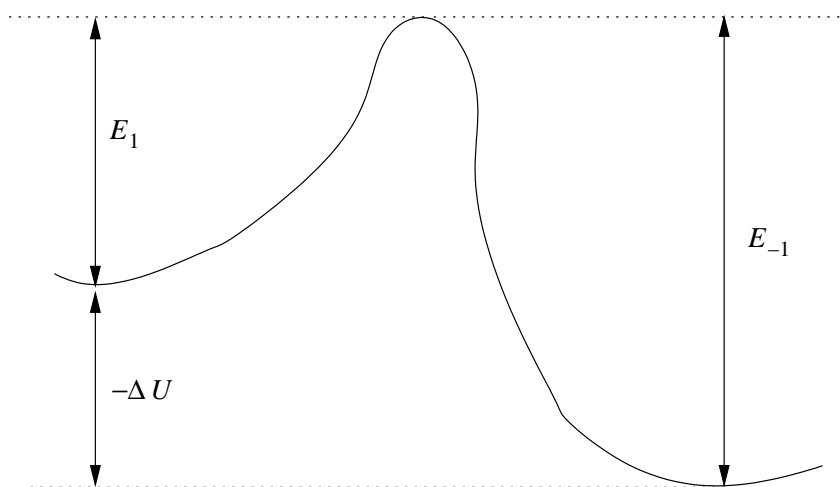


Chemistry 2850 Practice Test 3 Solutions

1. The half-life is the time it takes for the difference between the concentration at time t and the equilibrium concentration to drop to half its initial value.
2. In a relaxation experiment, we start with a system at equilibrium. We then make a rapid change in conditions which changes the equilibrium constant, and we follow the concentration as it moves toward the new equilibrium.
- 3.



In this case, ΔU is negative (which is why I show the size of the difference as $-\Delta U$ in my sketch).

4. There are a number of possible answers, but the most obvious one is that the two molecules might collide in the wrong orientation. For instance, in the reaction $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$, the hydrogen atom has to hit the H end of the HBr molecule, otherwise this reaction can't happen.
5. The entropy of activation is the difference in entropy between the transition state and the reactants of a reaction.
6. We need the concentration of the reactant A as a function of time:

	[A]	[B]
Initial	0.624	0
Change	$-2x$	x
At time t	$0.624 - 2x$	x

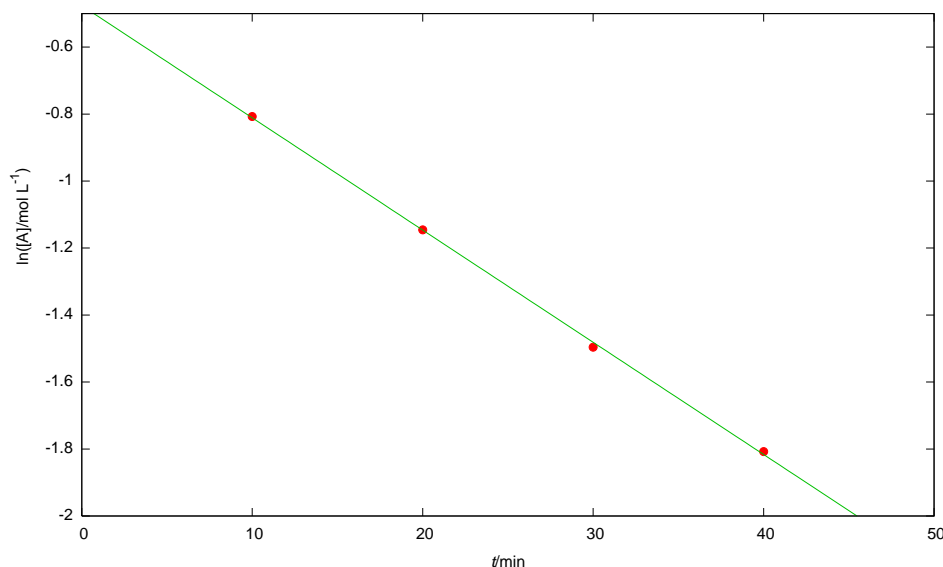


Figure 1: First-order plot for question 6.

Since $[B] = x$, we have

$$[A] = 0.624 - 2[B].$$

We can therefore construct the following table:

t/min	10	20	30	40
$[A]/\text{mol L}^{-1}$	0.446	0.318	0.224	0.164
$\ln([A]/\text{mol L}^{-1})$	-0.807	-1.146	-1.496	-1.808
$[A]^{-1}/\text{L mol}^{-1}$	2.242	3.145	4.464	6.098

Note: Many of you will be able to do the calculations of $\ln[A]$ and of $[A]^{-1}$ directly in your calculator as part of the process of obtaining the regression lines. In this case, you might not give a table of values for these quantities as I have done here, provide you explain in a few words what you did.

We can now draw our first and second order graphs, which are shown in figures 1 and 2. The first-order graph obviously looks linear while the second-order plot isn't. Accordingly, we can conclude that the reaction obeys first-order kinetics. The rate constant is the negative of the slope of this graph. By linear regression, we find a slope of -0.0335 min^{-1} , which corresponds to a rate constant of

$$k = 0.0335 \text{ min}^{-1}.$$

Important note: In a question like this one, you *must* draw both graphs to exclude the possibility that the data fits both rate laws equally well.

7. (a) We start by calculating T^{-1} and $\ln k$:

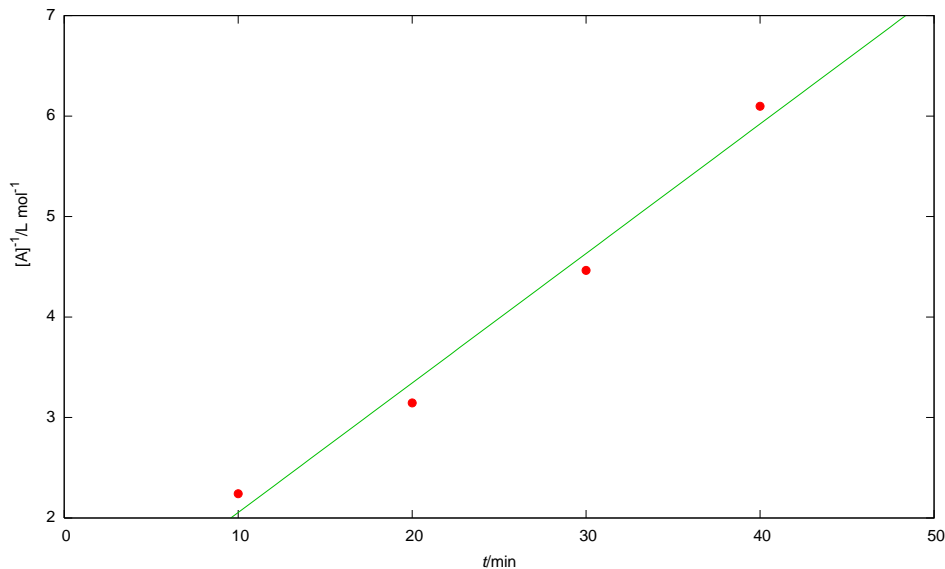


Figure 2: Second-order plot for question 6.

$T^{-1}/10^{-3}\text{K}^{-1}$	3.411	3.299	3.193	3.095	3.002	2.914
$\ln(k/\text{min}^{-1})$	-8.792	-8.454	-8.022	-7.545	-6.979	-6.567

Linear regression of the graph of $\ln k$ vs T^{-1} gives the following data:

$$\begin{aligned}\text{slope} &= -4590 \text{ K} = -\frac{E}{R} \\ \text{intercept} &= 6.744 = \ln A\end{aligned}$$

Therefore

$$\begin{aligned}E &= -(8.314\,472 \text{ J K}^{-1}\text{mol}^{-1})(-4590 \text{ K}) = 38.2 \text{ kJ/mol} \\ A &= e^{6.744} = 849 \text{ min}^{-1}\end{aligned}$$

(b)

$$\begin{aligned}\Delta^\ddagger H^\circ &= E - RT \\ &= 38.2 \text{ kJ/mol} - (8.314\,472 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(298.15 \text{ K}) \\ &= 35.7 \text{ kJ/mol} \\ A &= \frac{849 \text{ min}^{-1}}{60 \text{ s/min}} = 14.1 \text{ s}^{-1}. \\ \Delta^\ddagger S^\circ &= R \left[\ln \left(\frac{Ah}{k_B T} \right) - 1 \right] \\ &= (8.314\,472 \text{ J K}^{-1}\text{mol}^{-1}) \left[\ln \left(\frac{(14.1 \text{ s}^{-1})(6.626\,068\,8 \times 10^{-34} \text{ J/Hz})}{(1.380\,650\,3 \times 10^{-23} \text{ J/K})(298.15 \text{ K})} \right) - 1 \right] \\ &= -231 \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$