

CHEMISTRY 312 PHYSICAL CHEMISTRY
Homework Assignment # 2

1. The rate constant for a chemical reaction of the type $A + B \rightarrow \text{products}$ is found to obey the Arrhenius expression

$$k(T) = (10^{15} \text{ molecules}^{-1} \text{ m}^3 \text{ s}^{-1}) \times e^{-1515.4/T}.$$

Calculate ΔU^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger at 298 K.

Answer

The units of the pre-exponential factor have to be ignored in order to perform the required mathematical manipulations. From the relationships given in the text, we get

$$\begin{aligned}\Delta U^\ddagger &= E_a - RT = 10122 \text{ J mol}^{-1}. \\ \Delta H^\ddagger &= \Delta U^\ddagger + \Delta n^\ddagger RT = \Delta U^\ddagger - RT = 7644.4 \text{ J mol}^{-1}.\end{aligned}$$

To find ΔS^\ddagger , we use Eq. (9.101) and identify the pre-exponential factor to get

$$10^{15} = e^2 \left(\frac{k_B T}{h} \right) e^{\Delta S^\ddagger / R},$$

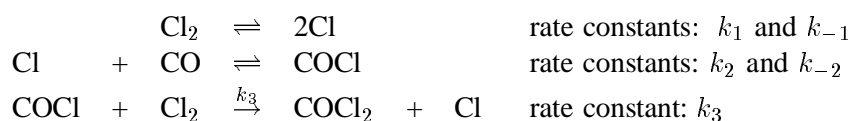
from which we get

$$\begin{aligned}\Delta S^\ddagger &= R \ln \left(\frac{10^{15} h}{e^2 k_B T} \right) \\ &= 25.621 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

Finally,

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger = 9.342 \text{ J mol}^{-1}.$$

2. The formation of phosgene by the reaction $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$ appears to follow the mechanism



Expressing the rate as the rate of formation of COCl_2 , derive a rate law for the reaction. [Assume that the steady state approximation can be applied to COCl and Cl .]

Answer

The rate expression is

$$\text{Rate} = k_3 [\text{COCl}] [\text{Cl}_2].$$

In order to substitute for the intermediate $[\text{COCl}]$, we use the steady state approximation. Applying the steady state approximation to $[\text{COCl}]$, we get

$$\frac{d[\text{COCl}]}{dt} = 0 = k_2 [\text{CO}] [\text{Cl}] - k_{-2} [\text{COCl}] - k_3 [\text{COCl}] [\text{Cl}_2], \quad (1)$$

from which we get

$$[\text{COCl}] = \frac{k_2 [\text{CO}] [\text{Cl}]}{k_{-2} + k_3 [\text{Cl}_2]}.$$

Applying the steady state approximation to [Cl], we get

$$\frac{d[\text{Cl}]}{dt} = 0 = k_1 [\text{Cl}_2] - k_{-1} [\text{Cl}]^2 - k_2 [\text{CO}] [\text{Cl}] + k_{-2} [\text{COCl}] + k_3 [\text{COCl}] [\text{Cl}_2]. \quad (2)$$

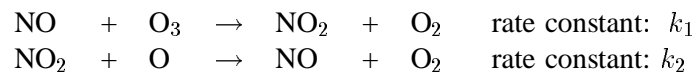
Adding Eqs. (1) and (2), we get

$$k_1 [\text{Cl}_2] - k_{-1} [\text{Cl}]^2 = 0, \text{ or} \\ [\text{Cl}] = \left(\frac{k_1}{k_{-1}} [\text{Cl}_2] \right)^{1/2}.$$

Substituting for [Cl] in the rate expression, we get the desired result:

$$\text{Rate} = k_3 \left(\frac{k_1}{k_{-1}} \right)^{1/2} \left(\frac{k_2}{k_{-2} + k_3 [\text{Cl}_2]} \right) [\text{CO}] [\text{Cl}_2]^{3/2}.$$

3. Ozone is decomposed by the catalytic reaction sequence



What is the steady state rate law for the formation of oxygen?

Answer

Rate law for the formation of oxygen is

$$\frac{d[\text{O}_2]}{dt} = k_1 [\text{NO}] [\text{O}_3] + k_2 [\text{NO}_2] [\text{O}].$$

Applying the steady state approximation to NO_2 , we get

$$\frac{d[\text{NO}_2]}{dt} = 0 = k_1 [\text{NO}] [\text{O}_3] - k_2 [\text{NO}_2] [\text{O}], \text{ or} \\ [\text{NO}_2] = \frac{k_1 [\text{NO}] [\text{O}_3]}{k_2 [\text{O}]}.$$

Substituting in the rate law, we get

$$\frac{d[\text{O}_2]}{dt} = 2k_1 [\text{NO}] [\text{O}_3].$$