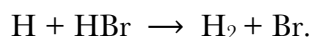


Dynamics and Kinetics. Exercises 11 & 12

Problem 1: TST rate constant

Use the transition-state theory to estimate the rate constant at 300K for the reaction



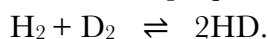
Barrier height (difference between zero-point energies of the transition state and reactants) is 5kJmol^{-1} . Molecule HBr has a bond length $d_{\text{H-Br}} = 141.4\text{ pm}$ and vibrational wave number $\tilde{\nu} = 2650\text{cm}^{-1}$. Assume the transition state to be linear with $d_{\text{H-H}} = 150\text{pm}$ and $d_{\text{H-Br}} = 142\text{pm}$ and with vibrational wave numbers $\tilde{\nu}_{\text{ss}} = 2340\text{cm}^{-1}$ (symmetric stretch) and $\tilde{\nu}_{\text{bend}} = 460\text{cm}^{-1}$ (two degenerate bending vibrations).

Problem 2: Pre-exponential factor

Estimate, on the basis of TST, the pre-exponential factor at 300K for a bimolecular gas-phase reaction between an atom and a diatomic molecule, with the formation of a linear transition state. Consider the translational partition functions to be 10^{32} m^{-3} , rotational partition functions for each degree of freedom to be 10, and the vibrational partition functions to be unity.

Problem 3: Equilibrium constant for isotopic change

Compute the equilibrium constant at 300K for the gas phase reaction



The vibrational wave numbers are 4371cm^{-1} for H_2 , 3786 cm^{-1} for HD , and 3092cm^{-1} for D_2 . The internuclear separation is 74pm for all three forms.

Problem 4: Entropy of activation

Two reactions of the same order have identical activation energies and entropies of activation differing by $50\text{JK}^{-1}\text{ mol}^{-1}$. What is the ratio of their rate constants (according to TST) at any temperature?

Problem 5: $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$

The gas-phase reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ is second order. Its rate constant at 400°C is $2.34 \times 10^{-2}\text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$ and its activation energy is 150kJmol^{-1} . Calculate, at 400°C , the standard enthalpy, entropy, and Gibbs free energy of activation (i.e., $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta G^\ddagger$), and the preexponential factor.