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

$$H + HBr \longrightarrow H_2 + Br.$$

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

$$H_2 + D_2 \rightleftharpoons 2HD.$$

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 50JK^{-1} mol^{-1}. What is the ratio of their rate constants (according to TST) at any temperature?

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

The gas-phase reaction H_2+$I_2 \longrightarrow$ 2HI is second order. Its rate constant at 400℃ is 2.34 x 10^{-2} dm^3 mol^{-1}s^{-1} and its activation energy is 150kJmol^{-1}. Calculate, at 400℃, the standard enthalpy, entropy, and Gibbs free energy of activation (i.e., $\Delta H^{\ddagger\circ}$, $\Delta S^{\ddagger\circ}$, $\Delta G^{\ddagger\circ}$), and the preexponential factor.