Problems for Collision Theory

1. Discuss at least three assumptions or approximations used to the frequency factor with collision theory. What are the limitations of collision theory?

2. List your approximations in developing the transition state theory (TST) and how seriously they will affect the estimate of the frequency factor. What are the limitations of TST?

3. What are the limitations to the polyani equation?

4. Write a few sentences describing activation energy and methods one can use to estimate it.

5. We are going to analyze the reaction between atomic fluorine and molecular hydrogen

$$F + H_2 \rightarrow HF + H$$

The reaction is carried out at 300K.
(1) Estimate the frequency factor A (dm^3/mol•s) using collision theory.

Additional information
  Reactants
    H–H Distance 0.74 Angstroms (Ang)
    H–H Stretch 4395 cm^{-1}
    H_2 Effective molecular diameter = 2.5 Angstroms
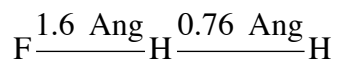   F   Effective atom diameter1.7 = Angstroms
    F = 19 amu
    H_2 = 2 amu

  Transition State
    Linear molecule
    Distances

$$F \xrightarrow{\text{1.6 Ang}} H \xrightarrow{\text{0.76 Ang}} H$$

    Vibrational Frequencies
    FHH   Bending 397 cm^{-1}
    FHH   Bending 392 cm^{-1} (degenerate)
    HH   Stretch 4007 cm^{-1}

  Constants
    k = Boltzmann's constant = 1.38 x 10^{-23} kg•m^2/s/molecule/K
    h = Plank's constant = 6.62 x 10^{-34} kg•m^2/s
    1 amu = 1.66 x 10^{-24} g
    1 kcal/mol corresponds to 350 cm^{-1}

  Other information that may or many not be useful
    $H_2 + Br \rightarrow HBr + H$ $E = 55.2 \dfrac{kJ}{mol}$

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Heats of Formation

HF   :   −272.55 kJ/mol
HCl :   −92.31 kJ/mol
HBr :   −36.44 kJ/mol
HI   :   26.36kJ/mol
H   :   218 kJ/mol
F   :   79.39 kJ/mol
Br   :   111.9 kJ/mol
I   :   106.8 kJ/mol
F_2 :   0 kJ/mol
H_2 :   0 kJ/mol