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

\[ \text{F + H}_2 \rightarrow \text{HF + H} \]

The reaction is carried out at 300K.

(1) Estimate the frequency factor \( A \) (\( \text{dm}^3/\text{mol} \cdot \text{s} \)) using collision theory.

Additional information

**Reactants**
- H–H Distance 0.74 Angstroms (Ang)
- H–H Stretch 4395 cm\(^{-1}\)
- \( \text{H}_2 \) Effective molecular diameter = 2.5 Angstroms
- F Effective atom diameter1.7 = Angstroms
- F = 19 amu
- H\(_2\) = 2 amu

**Transition State**
- Linear molecule
- Distances
  \[
  \begin{array}{c}
  \text{F} \\
  \text{H} \\
  \text{H}
  \end{array}
  \]

- 1.6 Ang
- 0.76 Ang

**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\( \cdot \)m\(^2\)/s/molecule/K
- \( h \) = Plank’s constant = 6.62 x \( 10^{-34} \) kg\( \cdot \)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**

\[ \text{H}_2 + \text{Br} \rightarrow \text{HBr} + \text{H} \]

\( E = 55.2 \) kJ/mol
Heats of Formation

HF : $-272.55 \text{ kJ/mol}$  
HCl : $-92.31 \text{ kJ/mol}$  
HBr : $-36.44 \text{ kJ/mol}$  
HI : $26.36 \text{ kJ/mol}$  
H : $218 \text{ kJ/mol}$  
F : $79.39 \text{ kJ/mol}$  
Br : $111.9 \text{ kJ/mol}$  
I : $106.8 \text{ kJ/mol}$  
F$_2$ : $0 \text{ kJ/mol}$  
H$_2$ : $0 \text{ kJ/mol}$