

Problems for Transition State Theory

1. 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?
2. We are going to analyze the reaction between atomic fluorine and molecular hydrogen



The reaction is carried out at 300K.

- (1) Estimate the activation energy E (kJ/mol)
- (2) Estimate the frequency factor A ($\text{dm}^3/\text{mol}\cdot\text{s}$) using transition state theory (TST). Before calculating A make a table showing each of the partition functions for each species (e.g., $q_V(\text{H}_2) \approx q_T(\text{H}_2) \approx q_V(\text{FHH}) \approx \dots$).
- (3) Compare and comment on the frequency factors calculated by these two methods.

Additional information

Reactants

H-H Distance 0.74 Angstroms (Ang)

H-H Stretch 4395 cm^{-1}

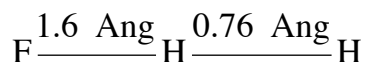
F = 19 amu

$\text{H}_2 = 2 \text{ amu}$

Transition State

Linear molecule

Distances



Vibrational Frequencies

FHH Bending 397 cm^{-1}

FHH Bending 392 cm^{-1} (degenerate)

HH Stretch 4007 cm^{-1}

Hint: It may speed your calculations if you take ratios for all partition functions. For example the transitional partition function ratio

$T = 300\text{K}$

$$\frac{q_{\text{FHH}}}{(q_{\text{H}_2})_T (q_{\text{F}})_T} = \frac{m^3 \frac{m_{\text{FHH}}^{3/2}}{1 \text{ amu}}}{9.89 \times 10^{29} \frac{m_{\text{H}_2}^{3/2}}{1 \text{ amu}} \frac{m_{\text{F}}^{3/2}}{1 \text{ amu}}}$$

Constants

$k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ kg} \cdot \text{m}^2 / \text{s} / \text{molecule} / \text{K}$

$h = \text{Plank's constant} = 6.62 \times 10^{-34} \text{ kg} \cdot \text{m}^2 / \text{s}$

$1 \text{ amu} = 1.66 \times 10^{-24} \text{ g}$

1 kcal/mol corresponds to 350 cm^{-1}

Other information that may or many not be useful



$$E = 55.2 \frac{\text{kJ}}{\text{mol}}$$

Heats of Formation

HF : -272.55 kJ/mol

HCl : -92.31 kJ/mol

HBr : -36.44 kJ/mol

HI : 26.36 kJ/mol

H : 218 kJ/mol

F : 79.39 kJ/mol

Br : 111.9 kJ/mol

I : 106.8 kJ/mol

F₂ : 0 kJ/mol

H₂ : 0 kJ/mol