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

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

The reaction is carried out at 300K.
(1) Estimate the activation energy E (kJ/mol)
(2) Estimate the frequency factor A ($dm^3/mol \bullet s$) using transition state theory (TST). Before calculating A make a table showing each of the partition functions for each species (e.g., $q_V(H_2) =$, $q_T(H_2) =$, $q_V(FHH) =$ ___).
(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
H_2 = 2 amu

Transition State

Linear molecule
Distances

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

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 = 300K

$$\frac{q_{FHH}}{(q_{H_2})_T (q_F)_T} = \frac{m^3 \left(\frac{m_{FHH}}{1\ amu}\right)^{3/2}}{9.89 \times 10^{29} \left(\frac{m_{H_2}}{1\ amu}\right)^{3/2} \left(\frac{m_F}{1\ amu}\right)^{3/2}}$$

Constants

k = Boltzmann's constant = 1.38×10^{-23} kg•m^2/s/molecule/K

h = Plank's constant = 6.62×10^{-34} kg•m^2/s

1 amu = 1.66×10^{-24} g

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

Other information that may or many not be useful

$H_2 + Br \rightarrow HBr + H$ $\qquad E = 55.2 \frac{kJ}{mol}$

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