Physical Chemistry III – Final report   Prof. Ji-Hyun Kim

1. Solve Problem 27-26, 27 on page 44 of the pdf material (refer to page 28). (10 points)

2. Solve Problem 27-49 on page 47 of the pdf material. (10 points)

3. Solve Problem 28-29 on page 87 of the pdf material. (10 points)

4. Solve Problem 28-33 on page 88 of the pdf material. (10 points)

5. The HF(*g*) *chemical laser* (light amplification by stimulated emission of radiation) is based on the reaction:

$$\mathrm{H_2}(g)+\mathrm{F_2}(g)\rightarrow 2\mathrm{HF}(g).$$

The mechanism for this reaction involves the following elementary steps:

		$\Delta_r H^\circ/\mathrm{kJ\cdot mol^{-1}}$ at 298 K
(1)	$\mathrm{F_2}(g)+\mathrm{M}(g)\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}2\mathrm{F}(g)+\mathrm{M}(g)$	+159
(2)	$\mathrm{F}(g)+\mathrm{H_2}(g)\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}\mathrm{HF}(g)+\mathrm{H}(g)$	−134
(3)	$\mathrm{H}(g)+\mathrm{F_2}(g)\xrightarrow{k_3}\mathrm{HF}(g)+\mathrm{F}(g)$	−411

Here, M is a certain nonreactive collision partner. HF lasers of high power (~5 MW) have been constructed. The laser is intended to be used either from a high-altitude plane or from a space station for military applications like destruction of missile. Answer the following questions.

(a) Estimate the bond dissociation energy, D_e, of H_2 in $\mathrm{kJ\cdot mol^{-1}}$ and comment on why the reaction, $\mathrm{H_2}(g)+\mathrm{M}(g)\rightarrow 2\mathrm{H}(g)+\mathrm{M}(g)$, is not included in the mechanism of the HF laser even though it produces a reactant that could participate in the reaction (3). (10 points)

(b) Derive the rate law for $d[\mathrm{HF}]/dt$ for the above mechanism assuming that the steady-state approximation can be applied to both intermediate species, F(g) and H(g), and discuss which condition is more favorable in order to prevent HF itself from reducing its production rate, $d[\mathrm{HF}]/dt$. (20 points)

(c) The reaction (2) and (3) are called cold and hot reactions, respectively, considering the relative magnitude of enthalpy release. The released energy can be converted into the vibrational energy of HF. In other words, the reaction (2) and (3) generate vibrationally excited HF molecules. Assuming i) the reactants and products are in their ground electronic states and ground rotational states, ii) H_2 and F_2 are in their ground vibrational states, and iii) the relative translational energy of the reactants is 15.0 $\mathrm{kJ \cdot mol^{-1}}$ for both reactions, determine the maximally allowed vibrational quantum numbers of HF produced by *the cold reaction and the hot reaction*. Treat the vibrational motions of H_2, F_2, and HF as harmonic with $\tilde{\nu}_{\mathrm{H_2}} = 4401.21\ \mathrm{cm^{-1}}$, $\tilde{\nu}_{\mathrm{F_2}} = 916.64\ \mathrm{cm^{-1}}$, and $\tilde{\nu}_{\mathrm{HF}} = 4138.32\ \mathrm{cm^{-1}}$. Recall that $\hbar\omega = h\nu = hc\tilde{\nu}$ with h and c denoting the Planck constant and the speed of light in vacuum, and refer to the energy diagram attached below for the cold reaction (see below for hints). (20 points)

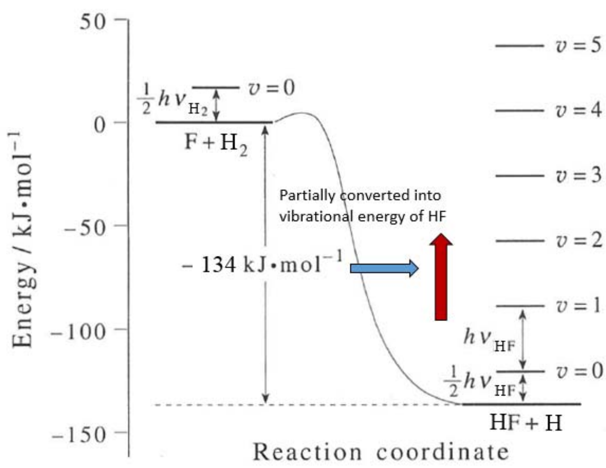
1) Use the fact that total energy for reactants is equal to total energy for products, i.e.,

$$E_{trans} + E_{vib} + E_{rot} + E_{elec} = E'_{trans} + E'_{vib} + E'_{rot} + E'_{elec}.$$

Here, you don't have to care about the kinetic energy associated to the center-of-mass velocity ($\mathbf{u}_{cm}, \mathbf{u}'_{cm}$) thanks to total mass conservation and total linear momentum conservation, e.g., for the cold reaction, $m_{\mathrm{F}} + m_{\mathrm{H_2}} = m_{\mathrm{HF}} + m_{\mathrm{H}}$ and $m_{\mathrm{F}}\mathbf{u}_{\mathrm{F}} + m_{\mathrm{H_2}}\mathbf{u}_{\mathrm{H_2}} = m_{\mathrm{HF}}\mathbf{u}_{\mathrm{HF}} + m_{\mathrm{H}}\mathbf{u}_{\mathrm{H}}$, leading to $\mathbf{u}_{cm}\left(= \frac{m_{\mathrm{F}}\mathbf{u}_{\mathrm{F}} + m_{\mathrm{H_2}}\mathbf{u}_{\mathrm{H_2}}}{m_{\mathrm{F}} + m_{\mathrm{H_2}}}\right) = \mathbf{u}'_{cm}\left(= \frac{m_{\mathrm{HF}}\mathbf{u}_{\mathrm{HF}} + m_{\mathrm{H}}\mathbf{u}_{\mathrm{H}}}{m_{\mathrm{HF}} + m_{\mathrm{H}}}\right)$ and $\frac{1}{2}(m_{\mathrm{F}} + m_{\mathrm{H_2}})\mathbf{u}_{cm} \cdot \mathbf{u}_{cm} = \frac{1}{2}(m_{\mathrm{HF}} + m_{\mathrm{H}})\mathbf{u}'_{cm} \cdot \mathbf{u}'_{cm}$.

2) When the zero of the electronic energy is taken to be separated atoms at rest in their ground electronic states, the ground electronic state energy for reactants (products) is given by $-D_e$ with D_e denoting the bond dissociation energy for the diatomic reactant (product) molecule.

3) In addition, note that the relative translational energy of the products must be positive.



(d) The laser is generated when the vibrational quantum number of HF drops by unity through the stimulated emission. Estimate the wavelength of the chemical laser in μm. (10 points)