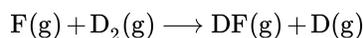


30.7: Reactions Can Produce Vibrationally Excited Molecules

As shown at the end of section 30.5, using the center of mass reaction model allows us to state that

$$E_{R(int)} + E_{R(trans)} = E_{P(int)} + E_{P(trans)} \quad (30.7.1)$$

where $E_{R(int)}$ and $E_{P(int)}$ represent the rotational, vibrational, and electronic energies collectively described as the internal energy of the reactants and the products, respectively. If we apply equation 30.7.1 to the well-studied gas-phase reaction



we can discuss the distribution of a fixed total collision energy between $E_{P(int)}$ and $E_{P(trans)}$. Specifically, if we assume that F(g) and D(g) are in their ground electronic states, that $\text{D}_2(\text{g})$ is in its ground rotational, vibrational, and electronic states, and that DF(g) is in its ground rotational and electronic states, we can focus on the possible vibrational states of the DF(g) that can be populated. Figure 30.7.1 shows the potential energy curve of the process that is described below.

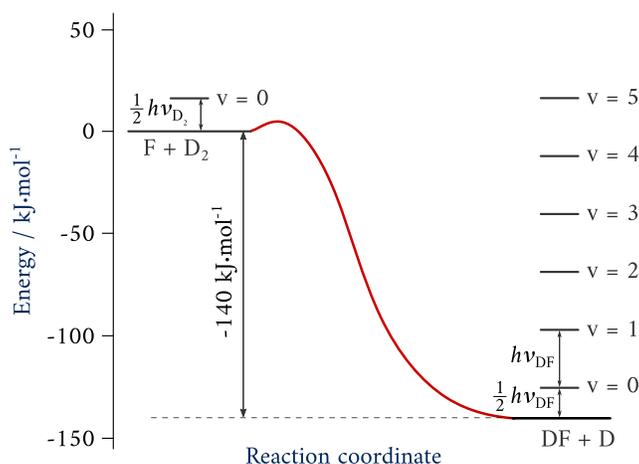


Figure 30.7.1: The potential energy diagram for the reaction $\text{F(g)} + \text{D}_2(\text{g}) \longrightarrow \text{DF(g)} + \text{D(g)}$ (CC BY-NC; Ümit Kaya via LibreTexts)

Expanding Equation 30.7.1 to describe this assumed process, we get

$$E_{R(rot)} + E_{R(vib)} + E_{R(elec)} + E_{R(trans)} = E_{P(rot)} + E_{P(vib)} + E_{P(elec)} + E_{P(trans)} \quad (30.7.2)$$

Let's assume that D_2 and DF are harmonic oscillators with $\tilde{\nu}_{D_2} = 2990 \text{ cm}^{-1}$ and $\tilde{\nu}_{DF} = 2907 \text{ cm}^{-1}$.

If D_2 and DF are in their ground electronic states, then $E_{R(elec)} = -D_e(\text{D}_2)$ and $E_{P(elec)} = -D_e(\text{DF})$. From experiments, we know that

$$-D_e(\text{DF}) - (-D_e(\text{D}_2)) = -140 \text{ kJ/mol}$$

We also know from experiments, that the activation energy for this reaction is about 6 kJ/mol^1 , so if we assume that the relative translational energy of the reactants is 7.1 kJ/mol , they will have sufficient energy to overcome the activation energy barrier.

With these data, we can write Equation 30.7.2 as

$$0 + E_{R(vib)} - D_e(\text{D}_2) + 7.1 \frac{\text{kJ}}{\text{mol}} = 0 + E_{P(vib)} - D_e(\text{DF}) + E_{P(trans)}$$

then

$$E_{R(vib)} + 7.1 \frac{\text{kJ}}{\text{mol}} = E_{P(vib)} + (-D_e(\text{DF}) - (-D_e(\text{D}_2))) + E_{P(trans)}$$

then

$$E_{R(vib)} + 7.1 \frac{kJ}{mol} = E_{P(vib)} - 140 \frac{kJ}{mol} + E_{P(trans)}$$

Because D_2 is in its ground vibrational state, $E_{R(vib)} = \frac{1}{2}h\nu_{D_2} = 17.9 \frac{kJ}{mol}$

Putting this altogether,

$$\begin{aligned} 17.9 \frac{kJ}{mol} + 140 \frac{kJ}{mol} + 7.1 \frac{kJ}{mol} - E_{P(vib)} &= E_{P(trans)} \\ 165 \frac{kJ}{mol} - E_{P(vib)} &= E_{P(trans)} \end{aligned} \quad (30.7.3)$$

Equation 30.7.3 tells us that the reaction will occur only if $E_{P(vib)}$ is less than 165 kJ/mol because $E_{P(trans)}$ must be a positive value.

If DF(g) is a harmonic oscillator, then

$$\begin{aligned} E_{P(vib)} &= \left(v + \frac{1}{2} \right) h\nu_{DF} \\ &= \left(v + \frac{1}{2} \right) (34.8 \text{ kJ/mol}) < 165 \text{ kJ/mol} \end{aligned}$$

Vibrational states, $v = 0, 1, 2, 3,$ and 4 will result in $E_{P(vib)} \leq 165$ kJ/mol. Thus DF(g) molecules in these five vibrational states will be produced by the reaction. Note that under these set of assumptions, the DF molecules produced in different vibrational states will have correspondingly different $E_{P(trans)}$.

¹Average of experimental E_a values listed at <https://kinetics.nist.gov/kinetics/> accessed 9/22/2021

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