Basic Kinetics

Reactive Collisions Between Molecules

ANSWERS

Objectives | Misconceptions | Comments

- To consider the orientation of the reactant molecules that is needed for a reaction to take place.
- To study the net thermochemistry of a reaction.
- To find the minimum amount of energy that is needed for successful reactive events.

Model

A *molecular beam* arises if a stream of gas expands from a reservoir into a low pressure chamber. If two such beams are made to intersect, this is a perfect setup for studying chemical reactions under highly controlled conditions. In this experiment, you will work with very simplified (single-molecule) molecular beams for the following reaction:

$$NO_2 + F_2 \longrightarrow NO_2F + F$$

The reaction is only the first one of a couple of steps that lead from the reactants to nitryl fluoride, but the other step will not be considered. The goal is specifically to gain a thorough understanding of the reaction step shown.

The simulation setup is shown on the left:

Run #1

For additional runs, request new initial configurations with the following control:

Fresh Initial Configuration

Questions

1. Start the simulation (below the model, select ▶). Does the initial configuration lead to the expected products?

   No, no reaction takes place.

2. Carry out a series of runs where you vary the relative *orientation* of the reaction partners:
   - Get a new initial configuration using the control above.
   - Select either one of the molecules. Reorient the chosen molecule (as opposed to reorienting the whole system):

     `Touchpad or Mouse:` With the cursor in the model area (!), hold down Ctrl and drag with the **left** button depressed.
     `Touchscreen:` Hold down Ctrl and drag with your finger.

   - When your modified initial configuration is ready, start the simulation (▶).
   - Carry out runs until you find a relative arrangement that leads to a successful reaction on impact.
   - *Note:* If you translate the reactants away from the collision course (in addition to reorienting them), they are likely to miss each other.

   Describe the arrangement that is associated with successful reaction events.

   Student answers may vary, but generally an arrangement should be found where the nitrogen and one the fluorines meet each other head-on upon collision.

3. Using your gained knowledge about how to induce successful reactions, now examine the energetics of the process (work with a fresh initial configuration):
   - Select  (or *View→Properties*).
   - From the **Add Property** menu (lower left corner), select **Energy ⟶ Total Energy (Molar)**.
   - Although labeled "total energy," the displayed value is really the sum of translational and vibrational energy of the two reactant molecules. Chemical bonding energy doesn't enter the picture because an energy scale is used where that energy happens to be zero.
   - The energy number is given for "1 mol of reactions as written" (see the reaction equation above). This is how chemists typically quote reaction energies and enthalpies.

   What is the total translational and vibrational energy of the system prior to the reaction?

   ~67.6 kJ/mol

4. The displayed energy value during the brief reaction event itself cannot be physically interpreted—it only reflect pecularities of the computational procedure. However, after completion of the reaction, the displayed energy value again has a physical meaning: it is the sum of translational and

vibrational energy of the molecules, now the *product* molecules. (Ignore the "total energy" label—just as prior to the reaction, chemical bonding energy is not accounted for, i.e., an energy scale is used, this time one appropriate for the products, where the bonding energy happens to be almost zero.)

What is the total translational and vibrational energy of the system after the reaction?

~130.6 kJ/mol

5. If the translational and vibrational energy of the product molecules is higher than that of the reactant molecules, we must be dealing with an exothermic reaction (= a reaction that releases energy). Conversely, if the translational and vibrational energy of the product molecules is lower than that of the reactant molecules, we must be dealing with an endothermic reaction (= a reaction that consumes energy). What type of reaction are you dealing with and what is the apparent energy change ΔE (in kJ/mol where "mol" is 1 mol of reactions)?

The translational and vibrational energy increases, so it must be an exothermic reaction:

$$\Delta E \approx -(130.6\text{-}67.6)\ \text{kJ/mol} = -63.0\ \text{kJ/mol}$$

(This is in fact the experimental value).

6. Next, determine the *minimum* amount of energy that needs to be put into the system for a reactive event to occur (work with fresh initial configurations):
   - Control the energy of the initial system using the **Slider** in the energy line of the *Properties* table, or edit the value field itself.
   - A good strategy to find the minimum energy required is to attempt a run with half of the original initial energy, then again with an energy at the halfway point of the interval just determined, etc.

   Give the minimum amount of energy required (within ±1 kJ/mol).

~44 kJ/mol (= the experimental value).

7. What is the technical term that represents the minimum energy that is needed for reactive events to take place?

Activation energy

8. Sketch an energy diagram that illustrates the overall energetics of the reaction. Put the "reaction coordinate" on the X axis and the energy on the Y axis. Annotate the drawing with the energies and energy differences that you have determined in this experiment.

(The graph should show the standard reaction profile for an exothermic reaction. At least two energy values should be explicitly shown: the energy difference between reactants and products, and the activation energy for the forward reaction.)

9. Consider a bulk sample with many molecules of nitrogen dioxide and many molecules of fluorine. Based on the observations in this experiment, how would you expect *temperature* to affect the rate of reaction between the two species?

The reaction rate will be sped up by increasing the temperature. That is, the number of reactions per unit time will increase with increasing temperature because a *larger fraction* of molecules will have sufficient energy to react. (In addition, the number of *collisions* will increase with temperature—an issue not touched on by this specific experiment.)

10. Would you attribute any temperature dependence to the the minimum energy requirements, the orientational requirements, or both?

Student answers will vary as this is a complex topic. The minimum energy requirements (activation energy) relate to temperature in a direct way via the *fraction* of molecules that carry enough energy to react (⟶ answer to the previous question).

In addition, the orientational requirements (steric factor) become less important with increasing temperature since molecules of higher energy simply have more venues to react (in terms of the potential energy surface, the "orientational requirements" are just areas of higher activation energies, thus molecules of higher energy have more ways to overcome the energetic barrier).

11. In a very general sense, would you expect "complexity" of the reactants to affect reaction rates? Would this be due to the orientational requirements or the minimum energy requirements?

In general one would expect that increased complexity of the reactants gives rise to more stringent orientational requirements and thus a changed reaction rate.