

Week 7

Gas-Phase Product Molecule Analysis and Intro to Lattices

7.1 Directional Scattering of the Product Molecule

5/9:

- The velocity and angular distribution of the products of a reactive collision.

– We have that

$$\begin{aligned} E'_{\text{trans}} + E'_{\text{vib}} &= E_{\text{trans}} + E_{\text{vib}} - [D_e(\text{D}_2) - D_e(\text{DF})] \\ &= 7.62 \text{ kJ mol}^{-1} + 17.9 \text{ kJ mol}^{-1} + 140 \text{ kJ mol}^{-1} \\ &= 166 \text{ kJ mol}^{-1} \end{aligned}$$

– Additionally, we know that

$$E'_{\text{trans}} + E'_{\text{vib}} = \frac{1}{2}\mu'u_r'^2 + (34.8 \text{ kJ mol}^{-1})\left(v + \frac{1}{2}\right) = 166 \text{ kJ mol}^{-1}$$

– The relationship between the vibrational quantum number, the relative speed of the products, and the speed of DF relative to the center of mass has been tabulated.

- A contour map of the angular and speed distributions for the product molecule.

– The contour plot.

- The center of mass is fixed at the origin.
- The dashed circles correspond to the maximum relative speeds a DF molecule can have for the indicated vibrational state.
- The product molecules preferentially scatter back in the direction of the incident fluorine atom, a scattering angle of $\theta = 180^\circ$.
- The arrows at the bottom of the figure show the direction with which each reactant molecule approaches the other.
- Another picture is provided, illustrating the atom-molecule reaction $\text{F} + \text{D}_2$ in which $\theta = 0^\circ$ and $\theta = 180^\circ$.
- The influence of rotation.
 - Large numbers of product molecules have speeds between the dashed circles.
 - The dash circles correspond to the case where there is internal energy only in the vibrational states of the molecule, in which case the rotational energy corresponding to these circles is $E_{\text{rot}} = 0$ with $J = 0$.

- If DF is produced in an excited rotational state, we would expect to observe a speed that has a value intermediate between two fo the dashed circles.
- Not all gas-phase chemical reactions are rebound reactions.
 - Consider the reaction

$$\text{K(g)} + \text{I}_2(\text{g}) \longrightarrow \text{KI(g)} + \text{I(g)}$$
 - The product diatomic molecule in this case (KI) is preferentially scattered in the forward direction along the direction of the incident K atom.
 - Consider the reaction

$$\text{O(g)} + \text{Br}_2(\text{g}) \longrightarrow \text{BrO(g)} + \text{Br(g)}$$
 - The product molecule BrO is forward and back scattered with equal intensity.
 - Both of these observations can be read off of the contour maps of the two reactions.

7.2 Potential Energy Surfaces

- 5/11: • The velocity and angular distribution of the products of a reactive collision.

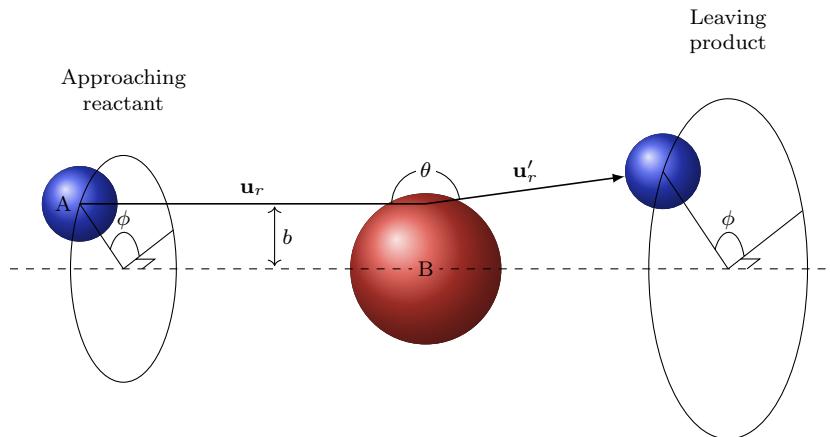


Figure 7.1: Velocity and angular distributions of the products.

- For a fixed value of the impact parameter b , the reactants and products take on all possible angles ϕ with equal probability, thereby forming a cone around the relative velocity vector \mathbf{u}_r .
- The angle θ , however, depends on the dynamics of the reaction and must be determined experimentally.
- The potential energy of a polyatomic molecule depends on more than one variable.
 - D_2 .
 - Consider the potential energy curve of D_2 . The zero of energy is defined to be that of the two separated atoms. The minimum of the potential energy curve corresponds to the equilibrium bond length of the D_2 molecule.
 - H_2O .
 - The potential energy of a water molecule is a function of the three parameters $r_{\text{O}-\text{H}_A}$, $r_{\text{O}-\text{H}_B}$, and α (two bond lengths and the interbond angle). In an equation,

$$V = V(r_{\text{O}-\text{H}_A}, r_{\text{O}-\text{H}_B}, \alpha)$$

- A plot of the complete potential energy surface of a water molecule therefore requires four axes.
 - The potential energy of a chemical reaction depends on more than one variable.

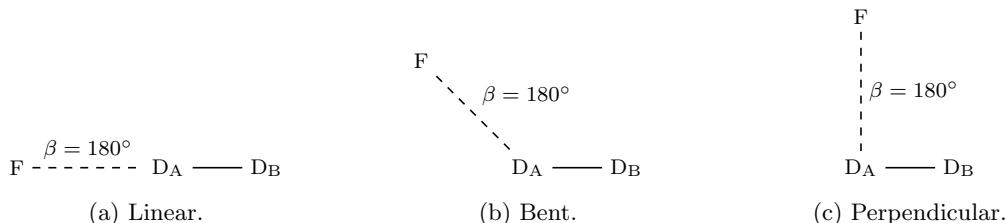
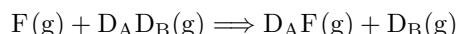


Figure 7.2: Angle of attack in $F + D_2$.

- Consider, once again, the reaction



- When the reactants are at infinite separation, there are no attractive or repulsive forces between the fluorine atom and the D₂ molecule, so the potential energy surface for the reaction is the same as that for an isolated D₂ molecule.
 - Likewise, when the products are at infinite separation, the potential-energy surface for the reaction is the same as the for the isolated DF molecule.
 - As the reaction occurs, however, the distance between the fluoroine atom and D_A decreases and the distance between D_A and D_B increases, and the potential energy depends on both distances.
 - The potential energy also depends on the angle at which the F atom approaches the D₂ molecule.
 - As with the angular and speed distributions, we can draw an energy contour map for the reaction.
 - The zero of energy is defined as the infinitely separated reactants. Point B is the location of the transition state of the reaction.
 - Tian does a brief summary of Chapter 30.

7.3 Lattice Structure

5/13:

- The unit cell is the fundamental building block of a crystal.
 - We can think of a crystal as a two- or three-dimensional lattice.
 - Either way, we can identify blocks in the lattice that form a regularly repeating structure.
 - **Face-centered cubic** (unit cell): The following unit cell. *Also known as FCC, cubic close-packing. Structure*

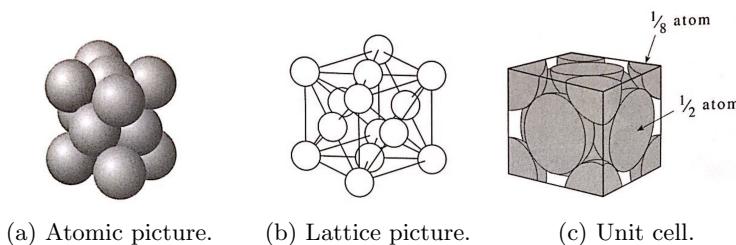


Figure 7.3: Face-centered cubic unit cell.

- Figure 7.3a shows the set of atoms that contribute to a unit cell of the crystal. The unit cell, itself, is a cube however (see Figure 7.3c).
- Figure 7.3b shows the unit cell for a three-dimensional lattice model of copper, where each point of the crystal is associated with a lattice point.
- Figure 7.3c shows the fractions of each copper atom shown in Figure 7.3a that contribute to the unit cell of the crystal.
- There are four atoms per unit cell (six half-atoms and eight eighth-atoms).
- Example: The packing of copper atoms in a copper crystal gives a face-centered cubic unit cell.

• **Body-centered cubic (unit cell):** The following unit cell. *Also known as BCC. Structure*

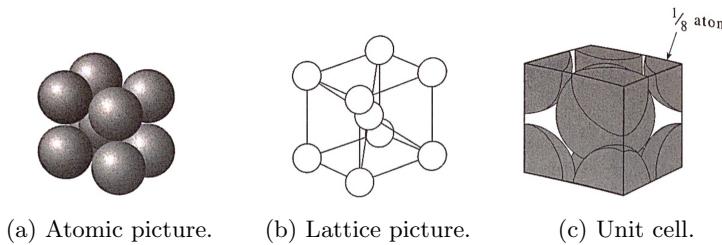


Figure 7.4: Body-centered cubic unit cell.

- There are two atoms per unit cell.
- Example: The packing of potassium atoms in a crystal.

• **Primitive cubic (unit cell):** The following unit cell. *Also known as simple cubic. Structure*

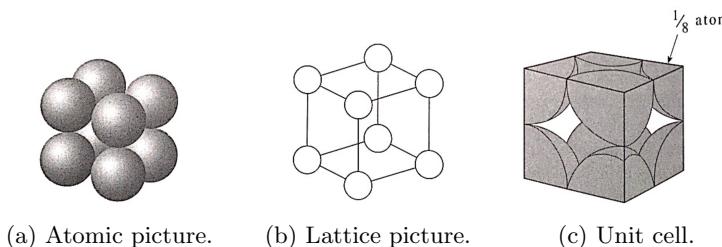


Figure 7.5: Body-centered cubic unit cell.

- There is one atom per unit cell.
- Example: The packing of polonium atoms in a crystal.

• **Unit cell:** The simplest repeating unit in the crystal. *Structure*

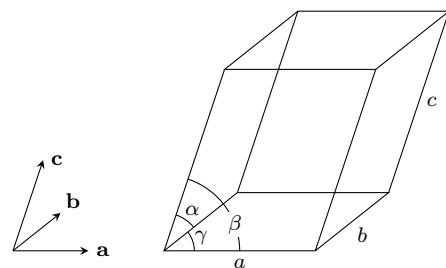


Figure 7.6: Unit cell.

- Opposite faces of a unit cell are parallel.
- The edge of the unit cell connects equivalent points.
- Unit cells all have the same general shape.
 - We take the bottom left corner of the unit cell to be the origin of the **a**, **b**, **c** coordinate system.
 - The unit cell is defined by the distances a , b , and c (which give its length along the **a**, **b**, and **c** axes, respectively) and the angles α , β , and γ (which lie between the three pairs of axes).
- Note that henceforth unless stated otherwise, the **a** axis points to the right, the **b** axis points back, and the **c** axis points up, as in Figure 7.6.
- Tian gives examples of unit cells for crystals containing more than one atom as well as what kinds of crystals take these structures.
- **Bravais lattices:** The fourteen distinct unit cells necessary to generate all possible crystal lattices.
 - The French physicist August Bravais proved that only the Bravais lattices are needed to generate all possible structures.
- We can interpret the points in the unit cell as atoms or molecules. For example, crystalline C_{60} forms a face-centered cubic unit cell.
- **Miller indices:** The three indices that we use to specify parallel planes through a crystal lattice. *Denoted by h , k , l . Given by*

$$h = \frac{a}{a'}$$

$$k = \frac{b}{b'}$$

$$l = \frac{c}{c'}$$

where the plane in question intersects the **a**, **b**, and **c** axes of the unit cell at points a' , b' , and c' , respectively.

- Three basic types of planes.

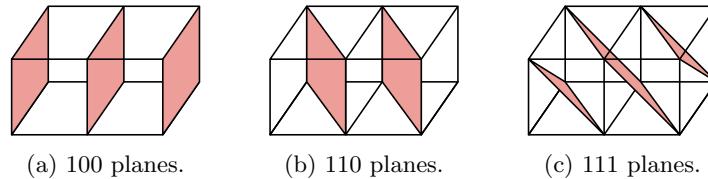


Figure 7.7: Basic lattice planes.

- Why are they called as such? Esp. where are the zeros coming from?
- Denoting more complicated types of planes.

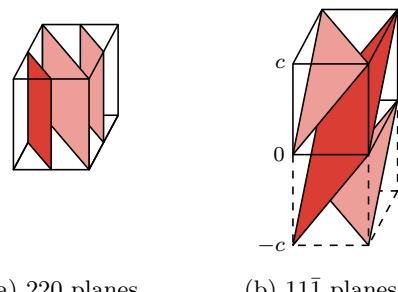


Figure 7.8: More complicated lattice planes.

- In Figure 7.8a, we denote by 220 the darkened plane and implicitly identify planes that are stacked twice as close together as in Figure 7.7b.
 - Note that $h = a/a' = a/(a/2) = 2$ and $k = b/b' = b/(b/2)$ is where the twos are coming from.
- In Figure 7.8b, we denote by 11 $\bar{1}$ the darkened plane. The $\bar{1}$ denotes a Miller index of *negative* one, corresponding to $c' = -c$ (notice how the darkened plane does not intersect the **c** axis within the unit cell, but rather extends down to the axis' negative region).
- The lattice plane spacing can be determined.
 - The perpendicular distance between adjacent hkl planes for an orthorhombic unit cell.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

– For a cubic unit cell,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

– For a tetragonal unit cell,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

– For a hexagonal unit cell,

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

– For a rhombohedral unit cell,

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

– For a monoclinic unit cell,

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

– For a triclinic unit cell,

$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

where

$$S_{11} = b^2 c^2 \sin^2 \alpha$$

$$S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma)$$

$$S_{22} = a^2 c^2 \sin^2 \beta$$

$$S_{23} = a^2 bc (\cos \beta \cos \gamma - \cos \alpha)$$

$$S_{33} = a^2 b^2 \sin^2 \gamma$$

$$S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta)$$

7.4 Chapter 30: Gas-Phase Reaction Dynamics

From McQuarrie and Simon (1997).

- 5/21:
- We will now build a molecular picture of the F + D₂ chemical reaction from the crossed molecular beam data. We take $E_{\text{react}} = 7.62 \text{ kJ mol}^{-1}$ throughout the following, as per the previous example.
 - The *angle* with which the molecules reach the detector.

- As per Figure 6.3 and the associated discussion, \mathbf{u}'_{DF} and \mathbf{u}'_{D} are not independent but are related by the conservation laws for mass, momentum, and energy.
- However, even though this means that DF and D could theoretically part ways in any manner consistent with these three laws, in reality, they will go their separate ways in some directions far more often than others, as dictated by the dynamics of this particular reaction.
- Let's consider these dynamics in greater detail, as facilitated by Figure 7.1.
 - In this picture, we take as our reference frame the perspective of spherically symmetric molecule B and let A approach.
 - For b fixed, the distribution in ϕ will be cylindrically symmetric.
 - However, the angle θ will vary.

5/22:

- The *speed* at which the molecules hit the detector.

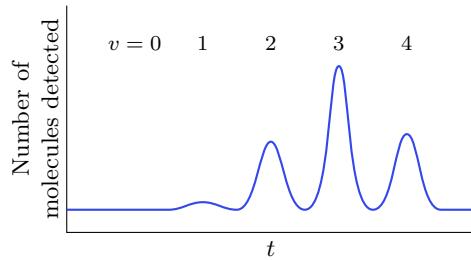
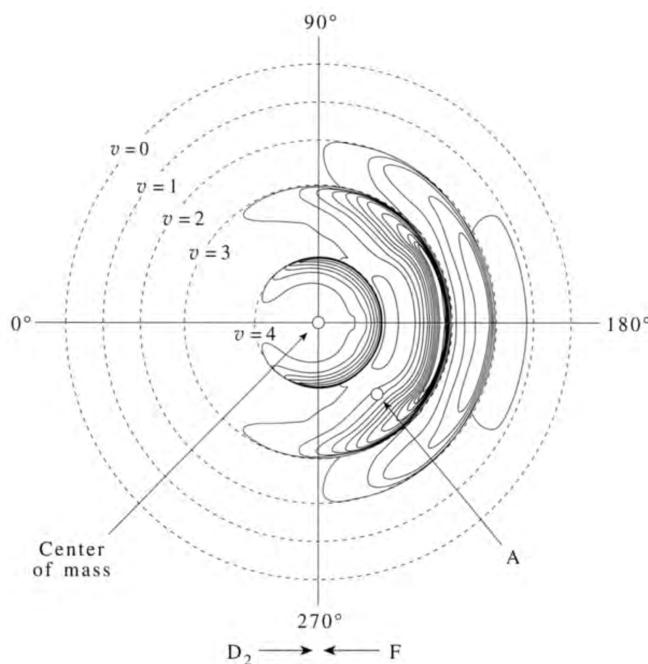


Figure 7.9: DF speed distribution.

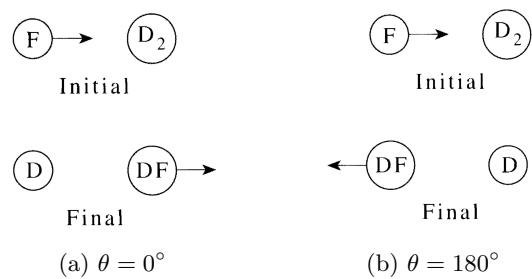
- Additionally, as per the previous example, DF can be produced in vibrational states zero through four.
- McQuarrie and Simon (1997) does a worked example, showing quantitatively how the speed of the DF molecule depends on its vibrational state.
- Experimentally, these results show up as separate peaks, each corresponding to a vibrational energy level, in Figure 7.9, which gives the collision frequency of DF molecules with the detector over time.
 - Notice that the molecules with the least vibrational energy have the most translational energy, and hence move the fastest and appear first.

5/24:

- We represent the distribution in angle and speed for a given reaction all at once with a 2D polar contour plot.
 - The center of mass (see Figure 6.3) sits at the center of the contour plot.
 - The arrows below the plot indicate the directions with which the reactants approached each other relative to the center of mass. In other words, the horizontal axis lies along the relative velocity vector of the reactants (see Figure 6.3).
 - The indicated angles correspond to the **scattering angle** θ (which is the complement of the angle θ from Figure 7.1).
 - The contour lines represent a constant number of DF molecules.
 - The dashed lines represent the maximum relative speed allowed for a DF molecule in a given vibrational state.
 - An increase in diameter corresponds to greater speed and lower vibration.
 - Note that all circles drawn correspond to rotational energy $E_{\text{rot}} = 0$ with $J = 0$. If a molecule is produced in a rotationally excited state, it must have a slower speed than the maximum allowed by its vibrational state. Consider a molecule located at position A in the diagram, for instance — for the molecule to have such a speed, it must either be rotationally excited, or have had more of the energy in its collision go into the translational energy of the other product (D).

Figure 7.10: Contour plot for $F + D_2$.

- **Scattering angle** (in an atom-molecule reaction): The angle between the relative velocity vector of the atomic reactant and the relative velocity vector of the product containing the formerly lone atom. Denoted by θ .
 - In $F + D_2$, the scattering angle is the change in the direction of the F -containing species. Indeed, since DF leaves the collision region in the same direction in which F entered in general, $\theta \approx 180^\circ$ in general for $F + D_2$, as is readily read from Figure 7.10.
- Further considerations of the scattering angle.

Figure 7.11: Scattering angles in the atom-molecule reaction $F + D_2$.

- Figure 7.11 shows the cases of $\theta = 0^\circ$ and $\theta = 180^\circ$ for $F + D_2$.
- Thus, the fact that DF preferentially scatters with $\theta \approx 180^\circ$ tells us that, in terms of Figure 6.3, we may have $A = F$ and $C = DF$ or vice versa so that the direction at which fluorine enters is the direction at which DF leaves; importantly, we do *not* have a case of $A = F$ and $D = DF$, in which the F -containing product leaves in the same relative direction at which the F -containing reactant entered.
- “In an atom-molecule reaction, we take $\theta = 0^\circ$ to lie along the direction defined by the trajectory of the incident atom” (McQuarrie & Simon, 1997, p. 1252).

- Relating Figure 7.10 to the crossed molecular beam experimental setup in Figure 6.4a.
 - In looking at Figure 7.10, imagine that we are located between the two molecular beam sources in Figure 6.4a and looking at the collision region. Let the blue molecules be D₂ and the red atoms be F (from our vantage point, this would make it look like F is coming in from the right and D₂ from the left, as in Figure 7.10). Additionally, the center of mass would not appear to be moving from our perspective because it would be moving away from us.
 - When two molecules collide, we would see (from our vantage point) molecules of DF exiting the collision region to the right more often than to the left; these molecules account for the preferential 180° scattering observed in Figure 7.10.
- Example: Determining the rotational state of point A in Figure 7.10.
 - It is determined that the DF molecule at point A has total rovibrational energy 11 493.6 cm⁻¹ and vibrational quantum number $v = 3$. Additionally, we find that

$$\begin{array}{cccc} \tilde{\nu}_e \text{ (cm}^{-1}\text{)} & \tilde{\nu}_e \tilde{x}_e \text{ (cm}^{-1}\text{)} & \tilde{B}_e \text{ (cm}^{-1}\text{)} & \tilde{\alpha}_e \text{ (cm}^{-1}\text{)} \\ \hline 2998.3 & 45.71 & 11.007 & 0.293 \end{array}$$

- From Chapter 13 and the above data, we have that

$$\begin{aligned} E_{\text{vib}}(v) &= \tilde{\nu}_e \left(v + \frac{1}{2}\right) - \tilde{\nu}_e \tilde{x}_e \left(v + \frac{1}{2}\right)^2 & E_{\text{rot}}(J, v) &= \left[\tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2}\right)\right] J(J+1) \\ &= 9934.1 \text{ cm}^{-1} & &= (9.982 \text{ cm}^{-1}) J(J+1) \end{aligned}$$

- Therefore,

$$\begin{aligned} E_{\text{tot}}(J, v) &= E_{\text{vib}}(v) + E_{\text{rot}}(J, v) \\ 11\,493.6 \text{ cm}^{-1} &= 9934.1 \text{ cm}^{-1} + (9.982 \text{ cm}^{-1}) J(J+1) \\ J(J+1) &= 156 \\ J &= 12 \end{aligned}$$

as desired.

- Three important features of the F + D₂ reaction, as determined from Figure 7.10.
 1. The reaction is a **rebound reaction**.
 2. The most probable product of the reaction is DF($v = 3$).
 3. There is considerable population between the dashed circles, indicating that DF molecules are produced in a variety of rotational levels.
- **Rebound reaction:** An atom-molecule reaction in which the atom undergoes a nearly head-on collision with the molecule and then bounces backward after abstracting one of the atoms from the molecule.
- Notice that the vibrational levels are populated in a distribution consistent with Figure 7.9, not the M-B distribution.
 - This is called a **nonequilibrium product distribution**.
 - We can use the Boltzmann factor to calculate the distribution in DF vibrational states at thermal equilibrium as follows.

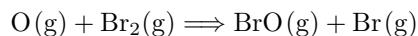
$$\frac{N(v)}{N(3)} = \frac{e^{-(v+1/2)h\nu_{\text{DF}}/k_B T}}{e^{-(3+1/2)h\nu_{\text{DF}}/k_B T}} = e^{-(v-3)h\nu_{\text{DF}}/k_B T}$$

- This reveals that the vibrational state v should be approximately 6(3 – v) orders of magnitude more populated than $v = 3$ at 300 K. In particular, $v = 0$ should be approximately 18 orders of magnitude more populated than $v = 3$ at said temperature, $v = 1$ should be approximately 12 orders of magnitude more populated than $v = 3$, and so on and so forth.

- **Stripping reaction:** An atom-molecule reaction in which the incident atom abstracts part of a molecule and keeps going in the forward direction.
- **Harpoon mechanism:** The mechanism by which a stripping reaction occurs, involving the formation of ions, followed by Coulombic attraction, followed by a reaction.
 - So named because the species which becomes a cation uses its electron as a “harpoon” to draw in (via the Coulomb potential) the species which becomes an anion.
- Evidence for the harpoon mechanism.
 - Consider the stripping reaction
$$\text{K(g)} + \text{I}_2\text{(g)} \longrightarrow \text{KI(g)} + \text{I(g)}$$

in which the relative translational energy between the reactants is $E_{\text{trans}} = 15.13 \text{ kJ mol}^{-1}$.

 - The contour plot shows a primary scattering angle of $\theta \approx 0^\circ$.
 - Thus, it would appear that electric fields are not repulsing the molecules as we would expect in a head-on collision.
 - The reaction cross section is twice the collision cross section.
 - We can measure the reaction cross section of $\text{K} + \text{I}_2$ to be $1.25 \times 10^6 \text{ pm}^2$.
 - Based on the measured radii of K and I_2 as 205 pm and 250 pm, respectively, we have that $\sigma_{\text{K I}_2} = 6.5 \times 10^5 \text{ pm}^2$.
 - Indeed, this means that if the reactants travel at the maximum impact parameter (see Figure 6.1), they would miss each other entirely but somehow still react.
 - An electron transfer occurs between the two reactants before they collide.
 - If two molecules are to react without touching, they must somehow be attracted to each other in manner strong enough to at least temporarily overcome the bond-dissociation energy (BDE) of the molecule.
 - Research shows that van der Waals interactions would not be strong enough for this, but a Coulomb potential would be.
 - Additionally, we can directly experimentally verify that this pre-reaction electron transfer occurs.
- Reactions in which the scattering angle is fairly equally distributed.
 - This cannot be either a hit-and-run collision or a drive-by collision.
 - Indeed, the only explanation is that lifetime of the atom-molecule complex is long compared with the rotation period, so that the reactants “forget” their initial orientation while reacting and then break apart in relatively random directions.
 - An example reaction that proceeds in this fashion is



- McQuarrie and Simon (1997) discusses the three variables that determine the potential energy surface of a water molecule and the analogous three variables that determine the potential energy surface of $\text{F} + \text{D}_2$.
- We can't represent these potential energy surfaces with a 2D- or 3D graph (we'd need four axes), so we have to turn to cross sections (i.e., fixing one of the variables and plotting the other two).
- The potential energy surface for a reaction can be computed using the electronic structure techniques of Chapter 11.
- **Collinear geometry:** A reactive collision with $\beta = 180^\circ$ (see Figure 7.2a).

- The potential energy surface for $\text{F} + \text{D}_2$ in a collinear geometry.

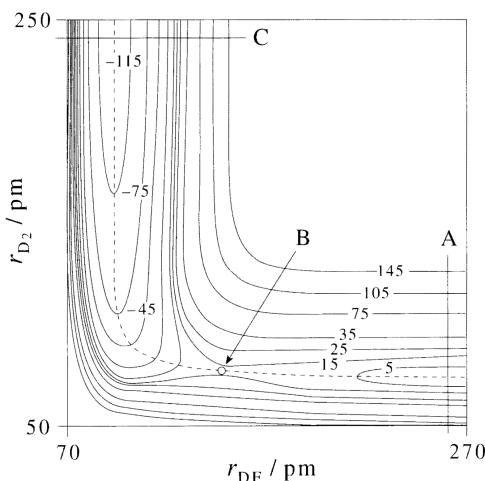


Figure 7.12: The potential energy surface for $\text{F} + \text{D}_2$ where $\beta = 180^\circ$.

- Each line in the contour map corresponds to a constant value of energy.
- The numbers on the lines express the energy of that line in kJ mol^{-1} .
- The zero of energy is taken to be the infinitely separated reactants.
- The cross section of the contour plot at A gives the potential energy curve for D_2 .
- The cross section of the contour plot at C gives the potential energy curve for DF.
- The dashed line proceeds from the bottom right to the top left and traces the reaction coordinate along the lowest-energy path.
- Point B indicates the transition state.
- Notice how as we trace the progress of the reaction, we start at energy near zero, climb the activation energy hill (passing the 5 kJ mol^{-1} contour but not quite reaching the 15 kJ mol^{-1} contour; the true value of the activation energy is approximately 7 kJ mol^{-1}), pass the transition state at a **saddle point**, and rapidly decrease in energy thereafter (this is an exergonic reaction).
- This diagram also gives meaning to the principle of microscopic reversibility, i.e., that a reaction (forwards or backwards) will always follow the lowest energy path.

7.5 Chapter 31: Solids and Surface Chemistry

From McQuarrie and Simon (1997).

- Goals of the chapter.
 - Solid-state chemistry: Crystal structure and how X-ray diffraction can be used to determine it.
 - Surface chemistry.**
 - Nitrogen fixation on iron catalysts.
- Surface chemistry:** The study of how the surfaces of solids catalyze chemical reactions.
- Looking at a crystal reveals a periodic structure that we should be able to take advantage of to describe its structure in general. To this effect, we define the **unit cell**.
- Unit cell:** The smallest collection of atoms (or molecules) in the crystal such that the replication of the unit cell in three dimensions generates the entire crystal.

- A unit cell cannot have any arbitrary shape.
 - A spherical unit cell would leave gaps, for instance.
 - It is also impossible to generate a crystal lattice by a unit cell that has a five-fold symmetry axis (see Problem 31-43).
 - Indeed, “the unit cell must be a geometric structure that fills all space when replicated” (McQuarrie & Simon, 1997, p. 1272).
- McQuarrie and Simon (1997) defines **face-centered cubic**, **body-centered cubic**, and **primitive cubic** unit cells.
- These are the only three types of cubic unit cells!
- McQuarrie and Simon (1997) develops a method of describing the most general type of unit cell (a three-dimensional parallelepiped) as in lecture (see the discussion associated with Figure 7.6).
- McQuarrie and Simon (1997) defines the **Bravais lattices**.

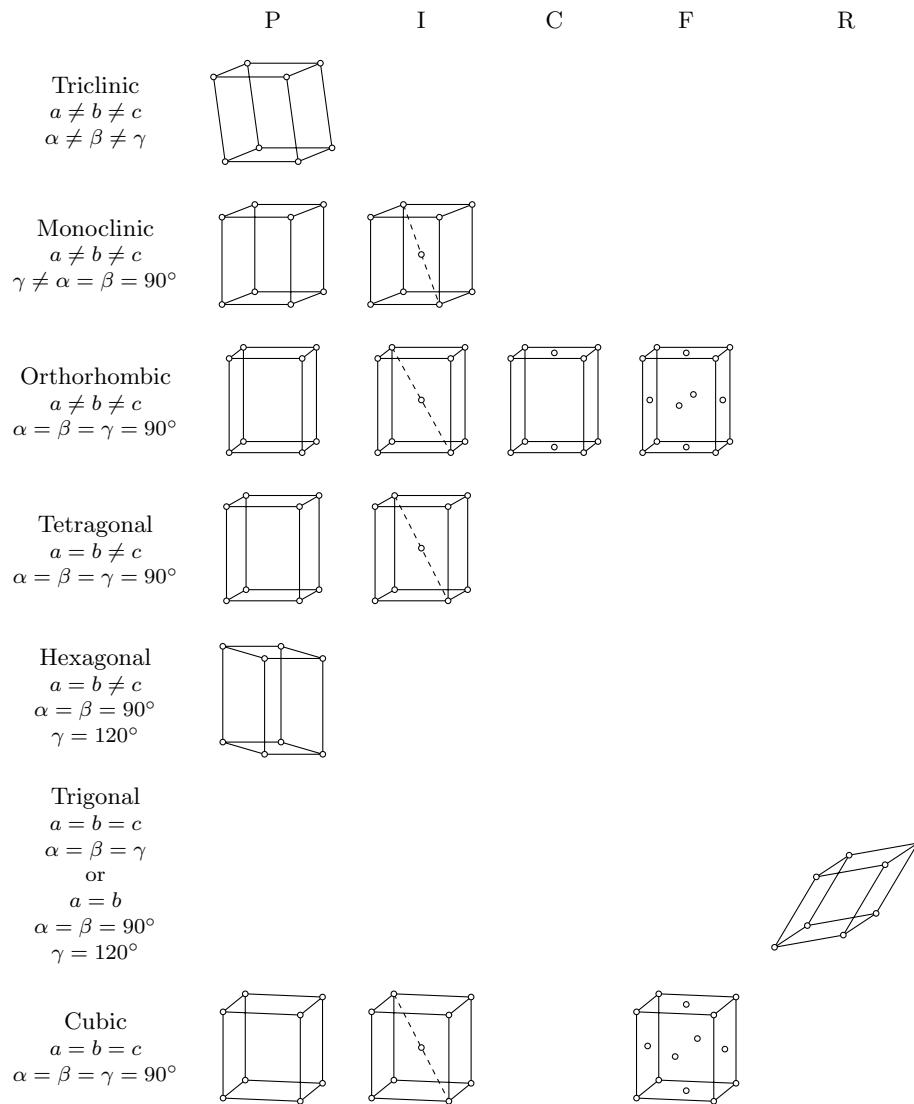


Table 7.1: Bravais lattices.

- What the column headings refer to.
 - P: Primitive unit cells (one lattice point per unit cell).
 - I: Body-centered unit cells.
 - C: End-centered unit cells.
 - F: Face-centered unit cells.
 - R: Rhombohedral unit cells.
- This chapter will focus on the Bravais lattices with orthogonal axes (i.e., for which $\alpha = \beta = \gamma = 90^\circ$).
- **Crystallographic radius:** The radius of the atoms of a substance in a crystal.
- Example: Calculating the crystallographic radius of copper, given that the density of copper at 20°C is 8.930 g cm^{-3} .
 - As per the discussion associated with Figure 7.3, there are four copper atoms to a unit cell. Additionally, the molar mass of a copper atom is 63.55 g mol^{-1} . Thus, the mass of a unit cell is
$$\text{mass unit cell} = \frac{(4)(63.55 \text{ g mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 4.221 \times 10^{-22} \text{ g}$$
 - It follows from the density that the volume of the unit cell is
$$V_{\text{unit cell}} = \frac{4.221 \times 10^{-22} \text{ g}}{8.930 \text{ g cm}^{-3}} = 4.727 \times 10^{-23} \text{ cm}^3$$
 - As per Figure 7.3c, the unit cell is cubic, so its side length is given by
$$a = (V_{\text{unit cell}})^{1/3} = 361.6 \text{ pm}$$
 - Also from Figure 7.3c, we can tell that the crystallographic radius of a copper atom is one-fourth the diameter of the unit cell. Therefore,
$$r = \frac{d}{4} = \frac{a\sqrt{2}}{4} = 127.8 \text{ pm}$$
- McQuarrie and Simon (1997) also goes through how to calculate, using simple geometry, the fraction of the volume of a unit cell occupied by atoms.
- McQuarrie and Simon (1997) discusses how the lattice points in a unit cell are simply mathematical constructs, and may therefore be identified with more than just atoms (e.g., whole molecules like C_{60}).
- We denote points in a unit cell by an ordered triple (a', b', c') where $a', b', c' \in [0, 1]$ describe how far from 0 to a , 0 to b , and 0 to c the point is along the **a**, **b**, and **c** axes, respectively.
 - For example, if we take the bottom-left corner of the body-centered cubic unit cell to be the origin (as in Figure 7.6), then we can read from Figure 7.4b that the coordinates of the nine lattice points are $(0, 0, 0)$, $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1, 1, 0)$, $(1, 0, 1)$, $(0, 1, 1)$, $(1, 1, 1)$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.
- The periodicity of a given lattice allows us to view it as being comprised of sets of equally spaced parallel planes containing lattice points.
 - We take this perspective in addition to the usual one because it will be advantageous when we get to X-ray diffraction.
- Describing a set of parallel crystallographic planes in terms of where they intersect a unit cell leads to the development of the **Miller indices**.
- The leftmost plane in Figure 7.7b intersects the **a** axis at 1, the **b** axis at 1, and are parallel to the **c** axis (or, from a naïve point of view, intersect the **c**-axis at ∞).

- Thus, we denote the planes by three indices $h = a/1a = 1$, $k = a/1a = 1$, and $l = c/\infty c = 1$.
 - We compress this notationally to 110.
- The Miller indices uniquely specify a set of parallel planes within a crystal, specifically those separated by a distance a/h along the **a** axis, b/k along the **b** axis, and c/l along the **c** axis.
 - McQuarrie and Simon (1997) goes through the examples in Figure 7.8.
 - McQuarrie and Simon (1997) gives the lattice plane spacing formulas for adjacent hkl planes in orthorhombic and cubic unit cells.

Problems

31-43. In this problem, we will prove that a crystal lattice can only have one-, two-, three-, four-, and six-fold axes of symmetry. Consider the following figure, where P_1 , P_2 , and P_3 are three lattice points, each separated by the lattice vector **a**. ...