Transition States. Coulomb’s Law and Electrostatics.

Friday, September 29, 2017
BME/CHE/PHY 558, Physical & Quantitative Biology
Rutgers University: Chemical Thermodynamics
Lecturer: Gábor Balázsi
Challenge: Energy landscapes versus rate constants

Consider the reaction: How do the reaction rates change?

\[ A \xrightarrow{f} B \xleftarrow{b} A \]

1. \( f_1 \? f \)
2. \( f_2 \? f \)
3. \( f_3 \? f \)

\[ k_f(T) = Ce^{\frac{-E_T-E_A}{kT}} \]
\[ k_b(T) = C'e^{\frac{-E_T-E_B}{kT}} \]

1. \( b_1 \? b \)
2. \( b_2 \? b \)
3. \( b_3 \? b \)

1. \( K_1 \? K \)
2. \( K_2 \? K \)
3. \( K_3 \? K \)
Energy landscapes versus rate constants

What if we increase the temperature?

Imbalances amplify.

Any $K > 1$ will increase.

Any $K < 1$ will decrease.

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<td>$f_1 &lt; f$</td>
<td>$f_2 = f$</td>
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$k_f(T) = Ce^{\frac{E_T - E_A}{kT}}$

$k_b(T) = C'e^{\frac{E_T - E_B}{kT}}$
Energy landscape and reaction coordinate

Chemical process vs. degrees of freedom define an energy landscape.

\[
D + H_2 \underset{k_r(T)}{\overset{k_f(T)}{\leftrightarrow}} HD + H
\]

HH bond breaks, HD bond forms (or vice versa)

Reaction coordinate $\xi$ is the path at the bottom of the valley.
Transition state theory

Assumption:
- intermediary state $I^\ddagger$ forms before reactants convert to products.

\[
K^\ddagger = \frac{[I^\ddagger]}{[A][B]} = \frac{k_f^\ddagger}{k_r^\ddagger}
\]

\[
\frac{dP}{dt} = k^\ddagger[I^\ddagger] = k^\ddagger K^\ddagger [A][B]
\]

We obtain the mass action law.

Rate coefficients relative to transition state: $k_f^\ddagger, k_r^\ddagger$
Reaction rate coefficient vs. energy levels

Macroscopic:

$A + B \xrightarrow{k_0} P$

Microscopic:

$k_0 = k^\ddagger \bar{K}^\ddagger = \frac{kT}{h} \left( \frac{q^\ddagger}{q_A q_B} \right) e^{\frac{\Delta D^\ddagger}{kT}} = \frac{kT}{h} \bar{K}^\ddagger$
Can valleys & barrier change independently?

\[ AB + C \xrightarrow{k} A + BC \]

\[ I^\dagger \]

\[ r_{AB} + r_{BC} = \text{const} \]

\[ r_{AB} = r \quad \text{=1 degree of freedom} \]

Assume: \( r_I \) is optimal & energy = proportional to \( (r - r_I) \):

\[ E_{AB}(r) = m_1(r - r_1) \]
The Evans-Polányi model

Linear dependence between $E_a$ & $\Delta G$

\[ \Delta G = E_{BC}(r_2) = m_2(r_2 - r^\ddagger) + E_a = m_2(r_2 - r_1) + \left(1 - \frac{m_2}{m_1}\right)E_a \]

\[ r^\ddagger = \frac{E_a}{m_1} + r_1 \]

\[ E_{AB}(r) = m_1(r - r_1) \]

\[ E_{BC}(r) = m_2(r - r^\ddagger) + E_a \]
Product stabilization speeds the reaction

Graphical model:
Lowering the valley on the right also lowers the activation energy.
Electric charge
Types of charges

Many elementary particles (protons, electrons) carry charge.

Charge can be either: positive (+) or: negative (-).

An object has net charge if its (+) and (-) charge contents differ.

+ +, - - (like charges) repel each other.

+ - (opposite charges) attract each other.
Coulomb’s Law

Experiments in the 1700s showed that charges act on each other with a force $f$ of magnitude:
- inversely proportional with the square of the distance between them, $r^2$.
- directly proportional with the magnitude of both charges, $q_1$ and $q_2$.

$$f = \kappa \frac{q_1 q_2}{r^2} \quad \text{where} \quad \kappa = \frac{1}{4\pi \varepsilon_0}$$

The unit of charge is: Coulomb (C).

$\varepsilon_0 = 8.85 \times 10^{-12} \text{F/m} = \text{permittivity of vacuum.}$
Electrostatic interaction energy

Assume that we have two charges, $q_1$ and $q_2$.

Their interaction energy = Work needed to bring one charge from $\infty$ to its current position:

$$u(r_{12}) = -\int_{\infty}^{r_{12}} f(r)dr = -\int_{\infty}^{r_{12}} \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2} dr$$

$$u(r_{12}) = -\frac{q_1 q_2}{4\pi\epsilon_0} \int_{\infty}^{r_{12}} \frac{dr}{r^2} = -\frac{q_1 q_2}{4\pi\epsilon_0 r_{12}}$$

The electrostatic interaction energy drops as inverse distance $1/r$:  
$$u(r) = -\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$
Electrostatic energy tells on stability of charge systems.

Imagine that we have 3 charges as indicated below. What makes this system stable? Their total interaction energy is:

\[ u = u_{1,2} + u_{1,3} + u_{2,3} \]

Will this system stay like this?
Electrostatic interactions can hold charges together.

Imagine that we have 3 charges as indicated below. What makes this system stable? Their total interaction energy is:

\[ u = u_{1,2} + u_{1,3} + u_{2,3} \]

\[ u = \kappa \frac{q_1 q_2}{r_{1,2}} + \kappa \frac{q_1 q_3}{r_{1,3}} + \kappa \frac{q_2 q_3}{r_{2,3}} = -2 \frac{\kappa q}{r} + \frac{\kappa}{2r} = \frac{\kappa(1 - 4q)}{2r} \]

\[ q > 1/4 \quad \Rightarrow \quad u < 0 \quad \Rightarrow \quad \text{The system is energetically stable} \]

\[ q < 1/4 \quad \Rightarrow \quad u > 0 \quad \Rightarrow \quad \text{The system is energetically unstable} \]
Electrostatic interactions hold ionic crystals together.

Unlike short-range bonds, electrostatic interactions act over long distances. They hold crystal structures together.

The electrostatic interaction energy of a NaCl crystal structure for 1 atom... Starting with Row 1:

$$u_{Row_1} = -\frac{2\kappa e^2}{a} + \frac{2\kappa e^2}{2a} - \frac{2\kappa e^2}{3a} + \ldots = -\frac{2\kappa e^2}{a} \ln(2) = -1.386 \frac{\kappa e^2}{a}$$

$$U_{ion \ in \ solid} = \sum_{i} u_{Row_i} = -1.747 \frac{\kappa e^2}{a}$$
Charge interactions in media

Some molecules can polarize (their positive and negative charges shift relative to each other).

The + charge will dominate on one side of the molecule, – charge will dominate on the other.

The reorientation of molecular dipoles modifies the force and interaction energy.

Are the forces larger or smaller in the dielectric?
Charge interactions are weaker in media

Some molecules can polarize (their positive and negative charges shift rel. to each other).

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Forces are smaller with the dielectric.
Charge interactions are weaker in media

In polarizable media, the potential becomes:

\[ u(r) = \frac{1}{4\pi \varepsilon_0} \frac{q_1 q_2}{D r} \]

\( D > 1 \) is the dielectric constant.
The more polarizable the medium, the larger \( D \).

Molecules could be:
- permanently polarized
- polarized when other charges are present.

Polarity of water molecules shield ionic interactions.
\( D_{\text{water}} = 78.54 \).
This is why salts ionize in water.
The Bjerrum length

The partition function with electricity contains terms of the form: \( e^{-\frac{u}{kT}} \)

When does \( kT \) dominate over \( u \)?

**Bjerrum length**: distance where Coulomb energy = Thermal energy for elementary charges.

\[
u = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{Dl_B} = k_B T \quad \Rightarrow \quad l_B = \frac{\kappa e^2}{Dk_BT} = \frac{\kappa N_A e^2}{DRT}
\]

The Bjerrum length for two electrons:

\[
l_B = \frac{(1.6 \times 10^{-19})^2}{4\pi 8.85 \times 10^{-12} \times 1.38 \times 10^{-23} \times 273}
\]

\[
l_B = 6.11 \times 10^{-8} \text{ m} = 611 \text{ Å}
\]

\( u(r) \)

\( kT \)

- Energy dominates
- Entropy dominates
Electrostatic forces as vectors

The electrostatic force acts along the line connecting two charges. Electrostatic forces add together as vectors. Vectors have magnitude and direction. Scalars have only magnitude.

\[ \mathbf{f} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2 \mathbf{r}}{Dr^2 r} \]

Components of a vector = Its projections on the axes of the coordinate system.

\[ f_x = f \cos(\alpha) \]
\[ f_y = f \sin(\alpha) \]

Other vectors:
- velocity
- torque
- surface vector = vector area
Vector addition

Add vectors = add their components, which become components of the vector sum.

\[ f_{\text{sum},x} = f_{1,x} + f_{2,x} = f_1 \cos(\alpha_1) + f_2 \cos(\alpha_2) \]

\[ f_{\text{sum},y} = f_{1,y} + f_{2,y} = f_1 \sin(\alpha_1) + f_2 \sin(\alpha_2) \]

The graphical method is to draw parallels with each vector.

The diagonal of the parallelogram is the vector sum.
The electrostatic field

The electrostatic field characterizes the space where charges exist.

At any point in space, it is defined as the force that would act on a unit (+1C) test charge.

\[ E(r) = \frac{1}{4\pi \epsilon_0} \frac{q_1}{D r_1^2} \frac{\mathbf{r}_1}{r_1} + \frac{1}{4\pi \epsilon_0} \frac{q_2}{D r_2^2} \frac{\mathbf{r}_2}{r_2} + \ldots \]  

(sum over all charges)
The electric field of a positive charge

The electric field of a positive point charge points radially away from the charge. It has spherical symmetry.

\[ E(r) = \frac{q}{4\pi \varepsilon_0 Dr^2} \frac{r}{r} \]

Garden hose or Vacuum cleaner in reverse: = analogy...

The electric field of a negative charge

The electric field of a negative point charge points radially towards the charge. It has spherical symmetry.

Water drain or vacuum cleaner analogy...

\[ E(r) = -\frac{q}{4\pi\varepsilon_0 Dr^2} \frac{r}{r} \]
The electric fields of charge pairs

Why do like charges repel each other?
Why do opposite charges attract?...

The electric field of a dipole has cylindrical symmetry.

Practice vector addition to map the field!

http://www.ribbonfarm.com/2015/06/23/where-do-electric-forces-come-from/
The electric field between two planar electrodes

The electric field between two parallel planar electrodes is linear.

Lettuce seeds floating in vegetable oil
The scalar (dot) product of two vectors

Dot product = the product of two vectors’ magnitudes with the cosine of their angle.

\[ \vec{n} \cdot \vec{v} = |\vec{n}| \cdot |\vec{v}| \cos(\theta) \]

Example:

The amount of fluid flowing through a surface element per unit time is proportional to the dot product of velocity \( \vec{v} \) and the area vector \((dS) \vec{n}\).