Chem 1B Midterm 2 Review

Jeffrey Nash

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1 Rate Laws

1.1 Finding Order of Reaction With Respect to an Individual Species

Finding the order of reaction with respect to each individual species in a reaction mechanism is crucial for finding the rate law for the overall reaction. Recall that the exponential coefficients x and y in the rate law reaction Rate $= k[A]^x[B]^y$ are NOT necessarily the coefficients on the products side of the reaction. In other words, for the reaction 2A + B → C corresponding to rate law $k[A]^x[B]^y$, x and y are **NOT** necessarily 2 and 1, respectively.

The rate law for each individual species must be found experimentally by changing the concentration of the species in question between two experiments while holding all concentrations constant. When we divide one experimental rate law by the other, we find that all factors held constant cancel out, and we are left with an equation that we can solve for the exponential coefficient corresponding to the species in question.

1.1.1 Example

Say we triple the concentration of A from 1 to 3 arbitrary units while holding B constant at 1 arbitrary unit. Experimentally, we observe that the rate doubles, going from 1 arbitrary unit to 2 arbutrary units.

The two equations describing this are:
$1 = k[1]^x[1]^y$ and $2 = k[3]^x[1]^y$

Dividing the first equation by the second, we see that the k and $[1]^y$ terms in each equation cancel out, and we are left with:
$\frac{1}{2} = (\frac{1}{3})^x$

Solving for [A]'s coefficient, then, is simply a matter of taking logarithms, rearranging the equation to isolate x, and rounding it to the whole number.

We repeat the same process for [B], making sure that we use two experiments where **only** B's concentration is changed, and solve for y.

1.2 Finding Overall Rate Law

Once we have solved for each coefficient in the rate law, we use the observed rates and concentrations from one of the experiments and solve for k. Plugging k back in gives us the rate law!

1.3 One Important Thing to Remember

Whether you have to solve for intermediates or not, the rate law for the products on the rate determining step (the 'slow' step) **is the law for the overall equation**.

1.4 Steady-State Approximation

Speaking of solving for intermediates, let's talk about steady-state approximation. Suppose we have a reaction with an overall mechanism:

$H_2(g) + I_2(g) \rightarrow 2HI(g)$ with corresponding rate law $\frac{d[HI}{dt} = k[H_2][I_2]$

However, the mechanism for the reaction is stated to be a two-step affair:

Step 1: $I_2 \rightleftharpoons^{k_1}_{k_{-1}} 2I\bullet$ (rapid equilibrium)

Step 2: $H_2 + 2I\bullet \rightarrow^{k_2} 2HI$ (slow).

The rate law for the equation involving H_2 and our desired product HI is described by the slow equilibrium and can be written as: $k_2[H_2][I\bullet]^2$

However, as one can see, the I radical ($2I\bullet$) is not in the overall equation and is cancelled out by being on the products side of first step and the reactants side of the second. We can use steady-state approximation to assume that $\frac{d[I\bullet}{dt} = 0$.

Additionally, **we know that the slow step will have a small k.**, and we can approximate this to be 0.

Writing out the equation, we have $\frac{d[I\bullet]}{dt} = k_1[I_2] - k_{-1}[I]^2 - \cancel{k_2[H_2][I]}^2$

The term with k_2, which is very small due to being associated with the slow-proceeding step, is eliminated from the equation because it is close to 0. We then solve for $[I\bullet]^2$ to get:

$[I\bullet]^2 = \frac{k_1[I_2]}{k_{-1}}$.

We plug this into the equation for the slow rate law, $k_2[H_2][I\bullet]^2$, to get one that matches the overall rate law. We redefine $\frac{k_1 k_2}{k_{-1}}$ as $k_{observed}$ when making this substitution.

2 Arrhenius Law

The Arrhenius equation is a formula for the temperature dependence of reaction rates. The equation is:

$$ln(k) = (-\frac{E_{act}}{R})(\frac{1}{T}) + ln(A) \tag{1}$$

where R is the gas constant: 8.314 J $mol^{-1}K^{-1}$, A is the pre-exponential factor, E_{act} is the activation energy, T is the temperature in degrees kelvin, and k is the rate constant dependent on temperature.

2.1 Pre-Exponential Factor

The pre-exponential factor describes the molecular geometry and collision theory of the reaction and is independent of temperature. It has to do with the shapes and interactions of the molecules that take place in the reaction. For example, two reactions involving a diatomic molecule and a free radical are likely to have similar A values, even if their k values and required activation energy (E_{act}) are different.

2.1.1 Collision Theory

Collision theory assumes that all molecules involved in the reaction are perfect spheres whose only source of energy is **kinetic** energy.

If the experimentally-determined pre-exponential factor A is **smaller** than that predicted by collision theory it implies that there are some restrictions to the reactions we did not consider.

If the experimentally-derived pre-exponential factor A is **larger** than that predicted by collision theory it implies that here are sources of energy we did not consider.

2.2 Activation Energy (E_{act})

Activation energy has to do with how much energy it takes to break the bonds of the reaectants so that the bonds for the products can be formed. Remember that, while energy is released when bonds are formed, you need to put in energy to break bonds.

2.3 How Pre-Exponential Factor and Activation Energy Affect Arrhenius Plots

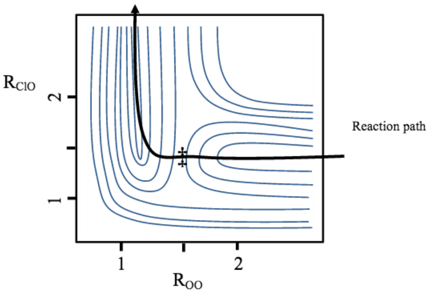
A higher required activation energy will result in a steeper negative slope. A higher pre-exponential factor will result in a higher y-intercept (the ln(A) term is larger).

3 Reaction Dynamics

3.1 Potential Energy Contour Plot

The below plot is a potential energy surface countour plot of the reaction:

$$ClO\bullet(g) + O\bullet(g) \rightarrow Cl\bullet(g) + O_2(g)$$



The above plot shows the bond radii, R_{ClO} and R_{OO} for the $ClO\bullet$ bond in the reactants side and the O_2 bond on the products side, respectively. The reaction path line shows the radius of each of these bonds throughout each step in the reaction, and the two crosses on the middle of this line denotes the transition state 'hump'.

3.1.1 Bond Length and Strength

From the data, it is clear that OO ends up with a shorter bond, and this bond, is, consequentially, stronger, due to higher attractive forces at shorter atomic radii.

3.1.2 Relative Energies of Products and Reactants

Because R_{OO} corresponds to O_2 on the products side and R_{ClO} corresponds to $ClO\bullet$ on the reactants side, we can make assumptions about relative energies of products and reactants. Because the bond length of the compound on the products side, O_2, is shorter than that of the compound on the reactants side, $ClO\bullet$, we know that the bond on the products side has is stronger.

We know that, the stronger a given bond, the more energy released during the formation of this bond. This means that potential energy was **higher** at the beginning (reactants), and much of it was lost when the bond was formed between the two O molecules to make O_2.