Chemical Kinetics in Situations Intermediate Between Usual and High Concentrations: Fuzzy-Motivated Derivation of the Formulas

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1. Chemical Kinetics: Usual Formulas

- Chemical kinetics describes the rate of chemical reactions.
- For usual concentrations:
  - the rate of a reaction between two substances A and B
  - is proportional to the product $c_A \cdot c_B$ of their concentration.
- Similarly, if we have a reaction

$$\mathrm{A} + \ldots + \mathrm{B} \to \ldots$$

  with three or more substances:
  - the rate of this reaction
  - is proportional to the products of the concentrations of all these substances $c_A \cdot \ldots \cdot c_B$.

2. How Formulas of Chemical Kinetics Are Usually Derived

- Molecules of both substances are randomly distributed in space.
- So, for each molecule of the substance A:
  - the probability that it meets a B-molecule
  - is proportional to the concentration c_B.
- If the molecules meet, then (with a certain probability) they get into a reaction.
- Thus, the mean number of reactions involving a given A-molecule is also proportional to c_B.
- The total number of A-molecules in a given volume is proportional to c_A.
- Thus, the total number of reactions per unit time is proportional to $c_A \cdot c_B$.

3. Case of High Concentrations

- When the concentrations are very high, there is no need for the molecules to randomly bump into each other.
- Indeed, these molecules are everywhere.
- So, as soon as we have molecules of all needed type, the reaction starts.
- In other words, in this case, the reaction rate is proportional to the concentration of the corresponding tuples.
- Thus, the reaction rate is proportional to the minimum $\min(c_A, \ldots, c_B)$ of all the input concentrations

$$c_A, \ldots, c_B.$$

4. Example

- The formula $\min(c_A, \ldots, c_B)$ can be easily illustrated on a similar relation between predators and prey.
- Let us throw a bunch of rabbits into a zoo cage filled with hungry wolves.
- Then each wolf will start eating its rabbit.
- This will continue as long as there are sufficiently many rabbits to feed all the wolves.
- When $c_R \geq c_W$, the number of eaten rabbits will be proportional to the number of wolves, i.e., to c_W.
- When there are few rabbits ($c_R < c_W$), the number of eaten rabbits is sim the number of rabbits c_R.
- In both cases, the reaction rate is proportional to $\min(c_R, c_W)$.

5. Use of High-Concentration Reactions

1) The high-concentration reaction rate indeed turned out to be very useful to describe biochemical processes.
2) In many cases, difficult-to-solve computational problems can be reduced to problems of chemical kinetics.

- We can then solve the original problem by simulating these reactions.
- To make simulations as fast as possible, it is desirable to simulate reactions which are as fast as possible.
- The reaction rate increases with the concentrations of the reagents.
- Thus, to speed up simulations, we should simulate high-concentration reactions.
- This simulation indeed speeds up the corresponding computations.

6. Problem

- We know the formulas for the usual and for the high concentrations.
- However, it is not clear how to compute the reaction rate for concentrations between usual and high.
- Both $r = c_A \cdot c_B$ and $r = \min(c_A, c_B)$ are particular cases of *t-norms* – "and"-operations in fuzzy logic.
- This is not a coincidence:
  - there is no reaction if one of the substances is missing, so $c_A = 0$ or c_B imply that $r = 0$;
  - his is exactly the property of a t-norm.
- Fuzzy t-norms have indeed been effectively used to describe chemical reactions.
- *Problem:* there are many possible "and"-operations, it is not clear which one to select.

7. Analysis of the Problem: General Case

- Let's analyze the problem to find the most appropriate "and"-operation.
- Two molecules get into a reaction only when they are close enough.
- When these molecules are close enough, then the reaction rate is proportional to $\min(c_A, c_B)$.

8. Case of Low Concentrations

- When *concentrations* are *low*, then, within each region, we have either zero or one molecule.
- The probability to have two molecules is very small (proportional to the square of these concentrations).
- This probability can thus be safely ignored.
- In this case, for each region, the reaction occurs if we have both an A-molecule and a B-molecule.
- The probability to have an A-molecule is $\sim c_A$.
- The probability to have a B-molecule is $\sim c_B$.
- The distributions for A and B are independent.
- Thus, the probability to have both A- and B-molecules in a region is equal to the product of these probabilities.
- This probability is thus proportional to the product of the concentrations $c_A \cdot c_B$.

9. Case of High Concentrations

- When the concentrations are high, then each region has molecules of both types.
- The average number of A-molecules in a region is proportional to c_A: equal to $k \cdot c_A$ for some k.
- Similarly, the average number of B-molecules in a region is equal to $k \cdot c_B$.
- So the average reaction rate is proportional to

$$\min(k \cdot c_A, k \cdot c_B) = k \cdot \min(c_A, c_B).$$

- The rate is thus proportional to $\min(c_A, c_B)$.
- This analysis leads us to the following reformulation of our problem.

10. Resulting Formulation of the Problem in Precise Terms

- Within a unit volume, we have a certain number r of "small regions".
- Small means that only molecules within the same region can interact with each other.
- We have a total of $N_A = N \cdot c_A$ A-molecules and $N_B = N \cdot c_B$ B-molecules.
- Each of these molecules is randomly distributed among the regions.
- So, it can be located in any of the r regions with equal probability.
- Within each region, the reaction rate is $\sim \min(n_A, n_B)$.
- The overall reaction rate is the *average* over all the regions.

11. Analysis of the Problem

- Based on the above description, the number of A-molecules in a region follows the Poisson distribution.
- For each value k, the probability to have exactly $n_A = k$ A-molecules is equal to $\Pr(n_A = k) = \exp(-\lambda_A) \cdot \dfrac{\lambda_A^k}{k!}$.
- The mean value of the Poisson random variable is λ_A.
- On the other hand, we have $N \cdot c_A$ A-molecules in r cells.
- So, the average number of A-molecules in a cell is equal to the ratio $\dfrac{N \cdot c_A}{r}$.
- Hence $\lambda_A = \dfrac{N \cdot c_A}{r} = c \cdot c_A$, where $c \stackrel{\text{def}}{=} \dfrac{N}{r}$.
- Similarly, $\Pr(n_B = k) = \exp(-\lambda_B) \cdot \dfrac{\lambda_B^k}{k!}$, with $\lambda_B = c \cdot c_B$.

12. Analysis (cont-d)

- The distribution for $n = \min(n_A, n_B)$ can be obtained from the fact that $n \ge k \Leftrightarrow (n_A \ge k \,\&\, n_B \ge k)$.
- Since A- and B-molecules are independently distributed, $\Pr(n \ge k) = \Pr(n_A \ge k) \cdot \Pr(n_B \ge k)$.
- $\Pr(n_A \ge k) = \sum\limits_{\ell=k}^{\infty} \Pr(n_A = \ell) = \exp(-\lambda_A) \cdot \sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_A^\ell}{\ell!}$.
- Similarly, $\Pr(n_B \ge k) = \exp(-\lambda_B) \cdot \sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_B^\ell}{\ell!}$, so:

$$\Pr(n \ge k) = \exp(-(\lambda_A + \lambda_B)) \cdot \left(\sum_{\ell=k}^{\infty} \frac{\lambda_A^\ell}{\ell!} \right) \cdot \left(\sum_{\ell=k}^{\infty} \frac{\lambda_B^\ell}{\ell!} \right).$$

- The expected value E can be now computed as

$$E = \sum_{k=0}^{\infty} k \cdot \Pr(n = k) = \sum_{k=1}^{\infty} \Pr(n \ge k); \text{ thus:}$$

13. Resulting Formula for the Reaction Rate

- The reaction rate is proportional to

$$E \stackrel{\text{def}}{=} \exp(-(\lambda_A+\lambda_B)) \cdot \sum_{k=1}^{\infty} \left(\sum_{\ell=k}^{\infty} \frac{\lambda_A^\ell}{\ell!}\right) \cdot \left(\sum_{\ell=k}^{\infty} \frac{\lambda_B^\ell}{\ell!}\right).$$

- For a reaction between three or more substances A + ... + B→ ..., we similarly get a formula

$$E = \exp(-(\lambda_A+\ldots\lambda_B))\cdot \sum_{k=1}^{\infty} \left(\sum_{\ell=k}^{\infty} \frac{\lambda_A^\ell}{\ell!}\right) \cdot \ldots \cdot \left(\sum_{\ell=k}^{\infty} \frac{\lambda_B^\ell}{\ell!}\right).$$

- These formulas can be simplified if we use the incomplete Gamma-function

$$\Gamma(s,x) \stackrel{\text{def}}{=} \int_x^\infty t^{s-1}\cdot \exp(-t)\,dt.$$

- For this function, $\exp(-\lambda)\cdot \sum_{\ell=0}^{s-1} \frac{\lambda^\ell}{\ell!} = \frac{\Gamma(s,\lambda)}{(s-1)!}$.

14. Formula Simplified

- *Reminder:* $\exp(-\lambda)\cdot\sum_{\ell=0}^{s-1}\frac{\lambda^\ell}{\ell!}=\frac{\Gamma(s,\lambda)}{(s-1)!}$.
- Since $\exp(\lambda)=\sum_{\ell=0}^{\infty}\frac{\lambda^\ell}{\ell!}$, we have $\exp(-\lambda)\cdot\sum_{\ell=0}^{\infty}\frac{\lambda^\ell}{\ell!}=1$, hence $\exp(-\lambda)\cdot\sum_{\ell=s}^{\infty}\frac{\lambda^\ell}{\ell!}=1-\frac{\Gamma(s,\lambda)}{(s-1)!}$.
- Thus, for two substances, we have:

$$E=\sum_{k=1}^{\infty}\left(1-\frac{\Gamma(k,\lambda_A)}{(k-1)!}\right)\cdot\left(1-\frac{\Gamma(k,\lambda_B)}{(k-1)!}\right).$$

- In general:

$$E=\sum_{k=1}^{\infty}\left(1-\frac{\Gamma(k,\lambda_A)}{(k-1)!}\right)\cdot\ldots\cdot\left(1-\frac{\Gamma(k,\lambda_B)}{(k-1)!}\right).$$

15. Analysis of the Above Formula: Case of Low Concentrations

- Here, $E \stackrel{\text{def}}{=} \exp(-(\lambda_A+\lambda_B))\cdot \sum\limits_{k=1}^\infty \left(\sum\limits_{\ell=k}^\infty \frac{\lambda_A^\ell}{\ell!}\right)\cdot\left(\sum\limits_{\ell=k}^\infty \frac{\lambda_B^\ell}{\ell!}\right).$
- When λ_A and λ_B are small, then $\exp(-(\lambda_A+\lambda_B))$ is approximately equal to 1.
- Also, terms proportional to λ_A^2 and to higher powers of λ_A can be safely ignored.
- So, $\sum\limits_{\ell=1}^\infty \frac{\lambda_A^\ell}{\ell!} \approx \lambda_A$ and $\sum\limits_{\ell=k}^\infty \frac{\lambda_A^\ell}{\ell!} \approx 0$ for $k>1$.
- Similarly, $\sum\limits_{\ell=1}^\infty \frac{\lambda_B^\ell}{\ell!} \approx \lambda_B$ and $\sum\limits_{\ell=k}^\infty \frac{\lambda_A^\ell}{\ell!} \approx 0$ for $k>1$.
- Thus, the above formula takes the form $E=\lambda_A\cdot\lambda_B$.
- Since $\lambda_A = c\cdot c_A$ and $\lambda_B = c\cdot c_B$, this means that in this case, the reaction rate is indeed $\sim c_A\cdot c_B$.

16. Case of High Concentrations

- The largest of the terms $\frac{\lambda_A^\ell}{\ell!}$ can be found if we approximate $\ell!$ by the usual Stirling approximation $\ell! \approx \left(\frac{\ell}{e}\right)^\ell$.
- Then, each term $\frac{\lambda^\ell}{\ell!}$ reduces to $\left(\frac{\lambda \cdot e}{\ell}\right)^\ell$.
- This term is the largest when its logarithm L is the largest: $L \stackrel{\text{def}}{=} \ell \cdot (\ln(\lambda) + 1 - \ln(\ell))$.
- Differentiating L with respect to ℓ and equating the resulting derivative to 0, we conclude that $\ell_0 = \lambda$.
- For this ℓ_0, the term $\frac{\lambda^{\ell_0}}{\ell_0!} = \left(\frac{\lambda \cdot e}{\ell_0}\right)^{\ell_0}$ turns into $\exp(\lambda)$.
- Since $\exp(\lambda) = \sum_{\ell=0}^{\infty} \frac{\lambda^\ell}{\ell!}$, this means that all terms $\ell \neq \ell_0$ in this sum are much smaller.

17. Case of High Concentrations (cont-d)

- *Reminder:* $\dfrac{\lambda^\ell}{\ell!} \ll \dfrac{\lambda^{\ell_0}}{\ell_0!}$ when $\ell \ne \ell_0$.
- Thus, all terms with $\ell \ne \ell_0 = \lambda$ can be ignored.
- We can therefore conclude that the ℓ_0-th term is equal to $\exp(\ell_0)$, while all other terms are 0s.
- So, $\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_A^\ell}{\ell!} = \exp(\lambda_A)$ when $\ell \le \lambda_A$, else $\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_A^\ell}{\ell!} = 0$.
- Also, $\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_B^\ell}{\ell!} = \exp(\lambda_B)$ when $\ell \le \lambda_B$, else $\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_B^\ell}{\ell!} = 0$.
- In $E \stackrel{\text{def}}{=} \exp(-(\lambda_A + \lambda_B)) \cdot \sum\limits_{k=1}^{\infty} \left(\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_A^\ell}{\ell!} \right) \cdot \left(\sum\limits_{\ell=k}^{\infty} \dfrac{\lambda_B^\ell}{\ell!} \right)$, only products with $\ell \le \min(\lambda_A, \lambda_B)$ are non-zeros.

18. Case of High Concentrations (cont-d)

- Here, $E \stackrel{\text{def}}{=} \exp(-(\lambda_A+\lambda_B))\cdot\sum\limits_{k=1}^{\infty}\left(\sum\limits_{\ell=k}^{\infty}\frac{\lambda_A^\ell}{\ell!}\right)\cdot\left(\sum\limits_{\ell=k}^{\infty}\frac{\lambda_B^\ell}{\ell!}\right)$, and only terms $\lambda \le \min(\lambda_A, \lambda_B)$ are non-zeros.
- For such terms,

$$\sum_{\ell=k}^{\infty}\frac{\lambda_A^\ell}{\ell!} = \exp(\lambda_A) \text{ and } \sum_{\ell=k}^{\infty}\frac{\lambda_B^\ell}{\ell!} = \exp(\lambda_B).$$

- So, each of the $\min(\lambda_A, \lambda_B)$ non-zero terms is equal to

$$\exp(-(\lambda_A+\lambda_B))\cdot\exp(\lambda_A)\cdot\exp(\lambda_B) = 1.$$

- So, their sum is indeed $\approx \min(\lambda_A, \lambda_B)$.

19. Remaining Open Questions

- Formulas similar to chemical kinetics equations are used in many different applications.
- *Examples:*
  - dynamics of biological species,
  - analysis of knowledge propagation.
- The above derivation of the intermediate "and"-operation uses the specifics of chemical kinetics.
- It would be interesting:
  - to perform a similar analysis in other applications areas and
  - to see which "and"-operations are appropriate in these situations.

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