Beyond Traditional Chemical Kinetics Formulas: Group-Theoretic Approach

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Abstract According to the traditional formulas of chemical kinetics, the rate is proportional to the product of concentrations of reagents. This formula leads to a reasonable description of interactions both in chemistry and in other disciplines (e.g., in ecology). However, in many cases, these formulas are only approximate. Several semi-empirical formulas have been designed to more accurately describe the interaction rate. The problem is that most of these formulas are purely empirical, they lack a convincing theoretical explanation. In this paper, we show that a group-theoretic approach – taking into account natural symmetries of the systems – leads to the desired theoretical explanation for these empirical formulas.

1 Formulation of the Problem

Traditional formulas of chemical kinetics. According to the traditional chemical kinetics formulas, the reaction rate is proportional to the product of the concentrations of all the inputs. In particular, for a reaction $\mathrm{A}+\mathrm{B}\to\mathrm{X}$, the rate is proportional to the product of the concentrations a and b of the substances A and B: $\frac{da}{dt}=g(a,b)$ and $\frac{db}{dt}=g(a,b)$, where $g(a,b)=-k\cdot a\cdot b$.

Chemical kinetics formulas are used to describe interactions beyond chemistry. Similar formulas are used to describe interactions in other areas as well. For example, in the standard Lotka-Volterra model of predator-prey interactions, the presence of predators P causes the decrease of the prey population N which is proportional to $N\cdot P$: $\frac{dN}{dt}=-k\cdot N\cdot P$; see, e.g., [10].

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Need to go beyond traditional formulas of chemical kinetics. In the first approximation, chemical formulas accurately describe interaction in chemistry and in other disciplines. However, more accurate measurements revealed that the actual reaction rate is somewhat different from the results obtains by the traditional formulas.

Traditional chemical kinetic formulas describe one-step reactions, when, e.g., the substances A and B directly interact and this interaction immediately leads to the quantity X. In practice, many chemical reactions are *multi-step* reactions. In such reactions, a direct reaction between the input substances A and B first leads to some intermediate substances, and only after several additional reactions involving this intermediate substance and/or A and B, we get the final quantity X. In such situations, even when each of the elementary reactions can be described by the traditional chemical kinetic formulas, the resulting dependence of the rate of change in A, B, and X on the initial concentrations of A and B becomes much more complex. Examples of complex functions describing such dependence are given in [6] (and references therein). In [5], it has been proven that any continuous function can be represented as a reaction rate for an appropriate multi-step chemical reaction system.

For many reactions, the dependence of the observed reaction rate on the initial concentrations is individual – in the sense that it is characteristic for this particular chemical reaction. For such reactions, the observed deviations from simple collision theory provide clues to the reaction mechanism that leads to the observed dependence; see, e.g., [6].

In addition to such *individualized* deviations from the simple chemical kinetic formulas, there are also *general* types of deviations, i.e., deviations which have the same form for many different chemical reactions. For example, Michaelis and Menten shows that for enzyme kinetics, the reaction rate is equal to $g(a,b) = \dfrac{c_0 \cdot a \cdot b}{1 + c_b \cdot b}$, for some constants c_0 and c_b. A similar formula describes the decrease of nutrient b as a function of the bacterial biomass a [7] and the decrease of prey b as a function of the predator concentration a [4].

This formula is also, in turn, only approximate; a more accurate description is provided by a more complex formula

$$g(a,b) = \frac{c_0 \cdot a \cdot b}{1 + c_a \cdot a + c_b \cdot b} \tag{1}$$

for some constants c_0, c_a, and c_b; see, e.g., [1, 2, 3, 9].

Problem. The problem with the general formulas describing non-standard chemical kinetics is that many of them – including the above formula (1) – are purely empirical, they lack a convincing theoretical explanation and thus, we are not sure whether (and why) they are indeed good approximations.

What we plan to do. In this paper, we use group-theoretic approach to provide a possible theoretical explanation for the above empirical formula (1).

2 Group-Theoretic Approach to the Problem: Main Idea

Different scales: general description. For many physical quantities, there are many different ways to describe their values. For example, temperature can be measured in degrees Fahrenheit, in degrees Celsius, or in degrees Kelvin; length can be measured in centimeters or in inches; time can be measured in seconds or in years; earthquakes can be measured by their energy or by a Richter scale (which is, in effect, a logarithm of this energy), etc.

Numerical values x and x' of the same quantity in different scales can be obtained from each other by an appropriate *re-scaling* $x' = f(x)$. For example, if we know the temperature t_C in Celsius, then we can compute the temperature t_F in Fahrenheit as $t_F = f(t_C)$, where $f(x) = 32 + 1.8 \cdot x$.

In general, if we have a scale x and a reasonable re-scaling transformation $f(x)$, then the values $x' = f(x)$ also form a reasonable scale for measuring the same quantity.

Reasonable re-scalings form a group. If a transition $f(x)$ from the scale x to a new scale $x' = f(x)$ is reasonable, then it seems natural that the inverse transformation from x' to x should also be reasonable. In other words, the class T of all reasonable transformations should contain, with each function $f(x)$, its inverse function $f^{-1}(x)$.

Similarly, if we start with a reasonable scale x, apply a reasonable transformation $x' = f(x)$, and then apply another reasonable transformation $x'' = g(x') = g(f(x))$, then the transformation $h(x) = f(g(x))$ should also be reasonable. In other words, the class T of all reasonable transformations should contain, for every two transformations $f(x)$ and $g(x)$, their composition $h = f \circ g$ which is defined as $(f \circ g)(x) \stackrel{\text{def}}{=} f(g(x))$.

It is well known that the composition operation is associative, that the identity mapping $i(x) = x$ has the property $f \circ i = i \circ f = f$ for all f, and that $(f \circ g)^{-1} = g^{-1} \circ f^{-1}$. In mathematical terms, this means that the class T of all reasonable transformations forms a *group* under composition.

Which groups are possible as groups of reasonable rescalings: physics-motivated requirements. In most cases, linear transformations are reasonable – they correspond to changing the measuring unit and the starting point. Thus, we are interested in groups which contain all linear transformations.

While non-linear transformations are physically possible, not all mathematical transformations are physically reasonable. For example, from the physical viewpoint, the transformations should be smooth (differentiable): indeed, smoothness is an important physical characteristics, and it should not depend on our choice of a scale.

An additional property is that if we have a sequence of reasonable transformations $f_n(x)$ that tend to a limit $f_n(x) \to f(x)$, this the limit $f(x)$ should also be a reasonable transformation. In mathematics, sets with such a property are known as *closed.* To be more precise, a set S is closed if for every sequence s_n of elements of the set S which tends to a limit $s_n \to s$, this limit s also belongs to the set S. In these terms, the above property means that the set T of all reasonable transformations should be *closed*.

Indeed, by definition of the limit, for any given accuracy, there exists an n for which $f(x)$ is (within this accuracy) indistinguishable from $f_n(x)$. From the physical viewpoint, if the limit transformation $f(x)$ cannot be distinguished from a reasonable one, no matter how accurately we measure, this means that the transformation $f(x)$ is also reasonable.

Finally, from the physical viewpoint, not all smooth mathematical functions describe physically reasonable transformations. Thus, it is reasonable to require that the class T differ from the class of all possible smooth functions from real numbers to real numbers.

Summarizing: we are looking for closed groups T of smooth functions which contain all linear transformations and which differ from the group of all smooth functions.

Which groups are possible as groups of reasonable rescalings: result. The complete description of all such groups T is known (see, e.g., [8]): each transformation $f(x)$ from each such group is *fractionally linear*, i.e., has the form $f(x) = \dfrac{c_0 + c_1 \cdot x}{1 + c_2 \cdot x}$ for some contants c_i.

From a general description to our specific problem. Let us apply the above general ideas to our problem.

In chemical reactions and in other types of interaction, it is reasonable to measure a concentration of a by the effect it has for some fixed b. For example, on scales, weight is measured by the pressure that a body with this weight makes on the given weighting scales.

In the interaction case, this means that while we can measure a directly, we can also measure it by the effect $g(a,b)$ that a has for a fixed value b. Thus, we have two reasonable scales a and $g(a,b)$. Therefore, the transformation $a \to g(a,b)$ between these two scales should be a reasonable transformation. We already know that reasonable transformations are fractionally linear; so, we conclude that for each b, the function $g(a,b)$ is a fractionally-linear function of a. Similarly, we can conclude that for each a, the function $g(a,b)$ is a fractionally-linear function of b.

In our case, we have two additional specific requirements:

- by the physical meaning of *interaction* between a and b, both substances need to be present for the interaction to occur; thus, if $a = 0$ or $b = 0$, we get $g(a,b) = 0$;
- if we increase both concentrations, the reaction rate should also correspondingly increase, i.e., we should have $g(a,b) \to +\infty$ if $a \to +\infty$ and $b \to +\infty$.

Let us now describe all functions $g(a,b)$ which satisfy these requirements.

3 Main Result

Proposition. *Let $g(a,b)$ be a function of two real variables which satisfies the following properties:*

- *for every b, the expression $g(a,b)$ is a fractionally linear function of a;*
- *for every a, the expression $g(a,b)$ is a fractionally linear function of b;*
- *if $a=0$ or $b=0$, then $g(a,b)=0$; and*
- *$g(a,b)\to\infty$ if $a\to\infty$ and $b\to\infty$.*

Then, the function $g(a,b)$ has the form

$$g(a,b)=\frac{c_0\cdot a\cdot b}{1+c_a\cdot a+c_b\cdot b} \tag{1}$$

for some constants c_0, c_a, and c_b.

Comment. It is easy to check that the specified conditions are satisfied if $g(a,b)$ has the given form (1). What needs to be proven is that the given form (1) of the function $g(a,b)$ is the only expression which satisfies these conditions.

Thus, this result indeed provides a group-theoretic justification of the above empirical formula for the reaction rate.

Mathematical comment. The first condition means that, when b is treated as a fixed parameter and a is treated as a variable, then $g(a,b)$ has the form

$$g(a,b)=\frac{c_0(a)+c_1(a)\cdot b}{1+c_2(a)\cdot b}, \tag{2a}$$

for appropriate functions $c_i(a)$. Similarly, the second condition means that when b is treated as a fixed parameter and a is treated as a variable, then $g(a,b)$ has the form

$$g(a,b)=\frac{d_0(b)+d_1(b)\cdot a}{1+d_2(b)\cdot a}, \tag{2b}$$

for appropriate functions $d_i(a)$.

Proof.

1°. As we have mentioned, the first condition means that for every a, the expression $g(a,b)$ is a fractionally linear function of b, i.e., that it has the form (2a) for appropriate functions $c_i(a)$.

2°. The condition that $g(a,b)=0$ for $b=0$ implies that $c_0(a)=0$, i.e., that

$$g(a,b)=\frac{c_1(a)\cdot b}{1+c_2(a)\cdot b}. \tag{3}$$

3°. Similarly, the second condition for $b=1$ and for $b=2$ means that the expression $g(a,b)$ is a fractionally-linear function of a, i.e., that

$$g(a,1)=\frac{N_1(a)}{D_1(a)} \text{ and } g(a,2)=\frac{N_2(a)}{D_2(a)} \tag{4}$$

for appropriate linear functions $N_b(a)=d_0(b)+d_1(b)\cdot a$ and $D_b(a)=1+d_2(b)\cdot a$.

4°. The condition that $g(0,1)=g(0,2)=0$ means that each linear function $N_i(a)$ is simply proportional to a, i.e., has the form $N_i(a)=n_i\cdot a$ for some real number n_i.

5°. Substituting the expression (3) into the formulas (4), we get

$$\frac{c_1(a)}{1+c_2(a)}=\frac{N_1(a)}{D_1(a)}; \tag{5}$$

$$\frac{2c_1(a)}{1+2c_2(a)}=\frac{N_2(a)}{D_2(a)}. \tag{6}$$

Multiplying each equation by the denominator of its left-hand side, we get

$$c_1(a)=c_2(a)\cdot\frac{N_1(a)}{D_1(a)}+\frac{N_1(a)}{D_1(a)}; \tag{7}$$

$$2c_1(a)=2c_2(a)\cdot\frac{N_2(a)}{D_2(a)}+\frac{N_2(a)}{D_2(a)}. \tag{8}$$

If we subtract, from the second equation (8), the first one (7) multiplied by 2, we get

$$2c_2(a)\cdot\left(\frac{N_2(a)}{D_2(a)}-\frac{N_1(a)}{D_1(a)}\right)+\left(\frac{N_2(a)}{D_2(a)}-\frac{2N_1(a)}{D_1(a)}\right)=0. \tag{9}$$

Multiplying both sides of this equation by $D_1(a)\cdot D_2(a)$, we get

$$2c_2(a)\cdot(N_2(a)\cdot D_1(a)-N_1(a)\cdot D_2(a))+(N_2(a)\cdot D_1(a)-2N_1(a)\cdot D_2(a))=0. \tag{10}$$

We can now take into account that $N_i(a)=n_i\cdot a$; thus, all the terms in (10) are proportional to a. So, we can divide both sides of the formula (10) by a and get

$$2c_2(a)\cdot(n_2\cdot D_1(a)-n_1\cdot D_2(a))+(n_2\cdot D_1(a)-2n_1\cdot D_2(a))=0. \tag{11}$$

Thus, we conclude that

$$c_2(a)=\frac{2n_1\cdot D_2(a)-n_2\cdot D_1(a)}{2\cdot(n_2\cdot D_1(a)-n_1\cdot D_2(a))}. \tag{12}$$

Both the numerator and the denominator of this formula are linear combinations of linear functions and are, thus, linear themselves. Therefore, the function $c_2(a)$ is fractionally linear, i.e., has the form

$$c_2(a)=\frac{c_{20}+c_{21}\cdot a}{1+c_{22}\cdot a} \tag{13}$$

for appropriate coefficients c_{2i}.

7°. Similarly, if we multiply both sides of the equation (7) by $2\dfrac{D_1(a)}{N_1(a)}$ and both sides of the equation (8) by $\dfrac{D_2(a)}{N_2(a)}$, we get

$$2\cdot\frac{D_1(a)}{N_1(a)}\cdot c_1(a)=2c_2(a)+2, \tag{14}$$

$$2\cdot\frac{D_2(a)}{N_2(a)}\cdot c_1(a)=2c_2(a)+1. \tag{15}$$

Substracting the second equation (15) from the first one (14), we conclude that

$$2\cdot c_1(a)\cdot\left(\frac{D_1(a)}{N_1(a)}-\frac{D_2(a)}{N_2(a)}\right)=1. \tag{16}$$

Multiplying both sides by $N_1(a)\cdot N_2(a)$, we conclude that

$$2\cdot c_1(a)\cdot(D_1(a)\cdot N_2(a)-D_2(a)\cdot N_1(a))=N_1(a)\cdot N_2(a). \tag{17}$$

Taking into account that $N_i(a)=n_i\cdot a$ and dividing both sides of (17) by a, we conclude that

$$2\cdot c_1(a)\cdot(D_1(a)\cdot n_2-D_2(a)\cdot n_1)=n_1\cdot n_2\cdot a, \tag{18}$$

hence

$$c_1(a)=\frac{n_1\cdot n_2\cdot a}{2\cdot(D_1(a)\cdot n_2-D_2(a)\cdot n_1)}. \tag{19}$$

Both numerator and denominator are linear functions (and the numerator has no free term), so the function $c_1(a)$ is also fractionally linear and has the form

$$c_1(a)=\frac{c_{11}\cdot a}{1+c_{12}\cdot a} \tag{20}$$

for appropriate coefficients c_{1i}.

8°. Substituting expressions (20) for $c_1(a)$ and (13) for $c_2(a)$ into the formula (3), we conclude that

$$g(a,b)=\frac{\dfrac{c_{11}\cdot a\cdot b}{1+c_{12}\cdot a}}{1+\dfrac{c_{20}+c_{21}\cdot a}{1+c_{22}\cdot a}\cdot b}. \tag{21}$$

9°. When $a,b\to\infty$, then for $c_{21}\neq 0$, we would have $g(a,b)\to\dfrac{c_{11}/c_{12}}{c_{21}/c_{22}}\neq\infty$. Thus, the requirement that $g(a,b)\to\infty$ implies that $c_{21}=0$. Hence, the formula (21) takes a simpler form

$$g(a,b)=\frac{\dfrac{c_{11}\cdot a\cdot b}{1+c_{12}\cdot a}}{1+\dfrac{c_{20}\cdot b}{1+c_{22}\cdot a}}. \tag{22}$$

10°. By adding the fractions in the denominator of the formula (22) and performing the division of the resulting fractions, we conclude that

$$g(a,b)=\frac{(c_{11}\cdot a\cdot b)\cdot(1+c_{22}\cdot a)}{(1+c_{12}\cdot a)\cdot(1+c_{22}\cdot a+c_{20}\cdot b)}. \tag{23}$$

In particular, for $b=1$, we get

$$g(a,1)=\frac{(c_{11}\cdot a)\cdot(1+c_{22}\cdot a)}{(1+c_{12}\cdot a)\cdot((1+c_{20})+c_{22}\cdot a)}. \tag{24}$$

11°. The expression (24) must be fractionally linear; thus, two linear forms in the numerator and in the denominator must cancel each other – by being either equal or proportional (differing by a multiplicative constant).

The expression $c_{11}\cdot a$ does not have a free term, while both factors in the denominator do. Thus, the only expression in the numerator which can cancel with some expression in the denominator is the expression $1+c_{22}\cdot a$.

There are two possibilities, let us consider them one by one.

11.1°. If the expression $1+c_{22}\cdot a$ cancels with the first factor $1+c_{12}\cdot a$, then $c_{22}=c_{12}$, and after canceling, we get

$$g(a,b)=\frac{c_{11}\cdot a\cdot b}{1+c_{22}\cdot a+c_{20}\cdot b}, \tag{25}$$

i.e., the desired expression (1).

11.2°. If the expression $1+c_{22}\cdot a$ cancels with the second factor $(1+c_{20})+c_{22}\cdot a$, this means that $c_{20}=0$. In this case, the formula (23) takes the form

$$g(a,b)=\frac{c_{11}\cdot a\cdot b}{1+c_{12}\cdot a}, \tag{26}$$

which is also a particular case of the desired expression (1).

In both cases, the have the desired expression (1). The proposition is proven.

Comment. Our proof is somewhat complicated. We believe that eventually, a simpler and clearer proof will be found.

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