



The units of rate constants in chemical kinetics

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Abstract

This short article discusses the units of rate constants as used in chemical kinetics and, in particular, the aspect of non-integral powers of base units, which some might find unusual for units in the SI system. In many ways the fact that the units of the rate constants as usually defined convey information about the order of the reaction or reactions involved is very useful, but in other ways having the same (or at least very similar) quantity that has different units under different conditions is not so desirable. Furthermore, just as with chemical equilibrium constants, taking functions of the rate constant (such as the logarithm when representing the Arrhenius equation in the form $\ln k$ vs. $1/T$) needs special attention. Here we examine a possible alternative definition of rate constants in terms of an explicit ratio to the concentration standard state and although we acknowledge that this approach unlikely to be adopted by the community, it serves as a basis to discuss the meaning of rate constants.

Keywords Units · Chemical kinetics · Rate constants · Dimensions

Introduction

The following thoughts were triggered by the discussion in the CODATA project on Digital Representation of Units of Measure (DRUM) [1] about the use of fractional powers for units, something that is not unusual in chemical kinetics, but not liked by some! Indeed, fractional powers are common for electromagnetic quantities in the cgs system [2] where there is no separate dimension for charge/current. In the SI

[3] most physical quantities can be expressed using only integral powers of the base SI units. We first examine the history and definition of the chemical reaction rate constant.

Rate constants

Following the formulation of a kinetic rate law as a differential equation involving powers of concentrations by Wilhelmy in 1850 [11], the Law of Mass Action postulated by Guldberg and Waage in 1864 [4, 5], is one of the key foundations of chemistry and states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants. The constant of proportionality is called the rate constant or rate coefficient. These ideas stem from the observation of the change in concentration of reactants or products with time and the slope of these functions giving the rate of the reaction as a function of time.

The rate of product formation or rate of loss of a reactant, in a chemical reaction has the unit of concentration per time. The concentration is typically an amount concentration, particle number density, or mass concentration (or several other related possibilities such as partial pressure, see the IUPAC Green Book [6]).

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If the reaction between species A and B to give product P, has a simple order, then we usually write,



and the rate of the reaction, v ,

$$v = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^n[B]^m[C]^x \quad (2)$$

where [P], [A], [B] are the concentrations of the product P and the species A and B from which it is formed, and n , m are the orders of the reaction with respect to A and B respectively, and x is the order with respect to C which may be some substance (atom or molecule), which does not appear in the stoichiometric equation, for instance a collision partner or catalyst (and in general there may be more than one of these).

Complex chemical reactions are usually built up from a sequence of elementary reaction steps. Elementary reactions are those for which no reaction intermediates have been detected or need to be postulated to describe the chemical reaction on a molecular scale.

Elementary reactions occur at the molecular level by a 'one step mechanism' as written, they are unidirectional and often identified with a single arrow \rightarrow as in Eq. (1) above.

Elementary reactions are commonly assumed to have a simple integer reaction order. They are described by their 'molecularity', which is related to the number of species appearing on the left hand side of the arrow in the reaction as written, and accordingly are called unimolecular, bimolecular or trimolecular, from the Latin sequence of prefixes uni-, bi-, tri-. We may note that for the last of these, frequently also 'termolecular' is used, with a less consistent etymology.

We note that even these simple statements hide a complexity of the chemistry. It is reasonable to envisage the collision of two gas phase species giving rise to a bi-molecular reaction (traditionally considered a theoretical microscopic idea, but now known to be an observable in crossed molecular beam experiments) which would then be expected to have a second order kinetics (which are macroscopically observable), The reaction order 2 for bimolecular reactions can be

theoretically justified by a probability argument considering the frequency of encounters of molecules in gases or condensed phases. For reactions in ideal gases a rigorous foundation can be obtained from statistical mechanics and quantum mechanical scattering theory [8]. For triple encounters relevant for trimolecular reactions the statistical probability is small at low densities and results in a reaction order 3. Higher molecularities than 3 are usually not considered because of their low probability.

More complex sequences of (elementary) reaction steps, at least in steady state approximations, resolve many of these issues and are typically discussed in the later years of an undergraduate chemistry degree. Solution, surface and solid state reactions present even more complexities when examined in detail. For a much more detailed discussion of rates for gas phase processes see the article by Luckhaus and Quack [8] from which the examples in Table 1 are also taken.

Unimolecular reactions need special consideration. They can occur as truly elementary processes such as in spontaneous radioactive decay or spontaneous emission of radiation from excited atoms or molecules, where a first order rate law applies in general, with a first order rate constant with the SI unit s^{-1} . However, thermal unimolecular reactions are not truly elementary processes in the strict sense but require a sequence of bimolecular energy transfer processes for instance with an inert collision partner M, which is either described with the simple Lindemann Hinshelwood mechanism or more generally a master equation [8] from which one can derive a steady state rate constant k_{uni} .

This model has two limiting cases. At high density (or pressure) of M the effective unimolecular rate constant is independent of the pressure or concentration of M and the reaction order is 1 with a rate constant k_{∞} . At low concentrations of M the rate constant is proportional to the concentration of M and thus the reaction order is 2, one can write

$$v = k_0[M][\text{reactant}] \quad (3)$$

Between these limits the rate constant depends on M with a variable power $[M]^m$ where $0 < m < 1$. This is an example

Table 1 Examples of the rate law, reaction order and rate constant units adapted from [8]

Reaction type	Reaction	Conditions	Rate law	Reaction order	Example units
Isomerisation	$CH_3NC = CH_3CN$	In excess inert gas	$-\frac{d[CH_3NC]}{dt} = k[CH_3NC]$	1st order in CH_3NC and overall first order	s^{-1}
Atom transfer	$F + CHF_3 = HF + CF_3$		$-\frac{d[F]}{dt} = k[CHF_3][F]$	1st order in F and CHF_3 2nd order overall	$dm^3 mol^{-1} s^{-1}$
Radical recombination	$CH_3 + CH_3 = C_2H_6$	In excess inert gas	$-\frac{1}{2} \frac{d[CH_3]}{dt} = k[CH_3]^2$	2nd order in CH_3 and overall	$dm^3 mol^{-1} s^{-1}$
Chain reaction	$CH_3CHO = CH_4 + CO$		$-\frac{d[CH_3CHO]}{dt} = k[CH_3CHO]^{3/2}$	Order 3/2 in CH_3CHO and overall	$dm^{3/2} mol^{-1/2} s^{-1}$

of a reaction order with some fractional or in general real value (see Ref [8]).

$$v = k[M]^m[\text{reactant}] \quad (4)$$

Frequently used units for concentration in chemistry would be amount of substance per volume (e.g. mol dm⁻³) or number of molecules per volume (molecule cm⁻³) or in chemical engineering often mass per volume (e.g. kg m⁻³) and the time scale can be anything from femtoseconds to millions of years or longer. We note that while molecule is not a unit recognized by the SI, it is often included for clarity although it is also frequently omitted, using the unit cm⁻³ for concentration. The IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation [7] provides recommended rate constants for bimolecular and termolecular elementary gas phase reactions in units of cm³ molecule⁻¹ s⁻¹ and cm⁶ molecule⁻² s⁻¹ or equivalently cm³/s and cm⁶/s.

In many cases the rate laws do not even have this simple power law form. Indeed the archetypal reaction of hydrogen with bromine:



has an empirically determined rate law in the form

$$\text{rate} = \frac{1}{2} \frac{d[\text{HBr}]}{dt} = \frac{k_1[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + k_2 \left(\frac{[\text{HBr}]}{[\text{Br}_2]} \right)} \quad (6)$$

As noted above, the chemistry community generally defines the kinetics in terms of the concentrations of the species involved, largely because we think about the collisions between the species and count the rate at which these occur. In contrast, equilibria are expressed in terms of species chemical activities which can take into account possible non-ideal behaviour.

The rate Eqs. (1) and (2) show that the units of the rate constant depend on the order of the reaction (or the effective order of each part of the expression in the more complex rate laws). This is often used as an example of how dimensional analysis can be useful in understanding or deducing the order of the reaction from the units of the rate constant, and students frequently find this a useful way to approach problems in chemical kinetics.

However, for many this leads to the fact that for non-integral reaction orders we end up with fractional exponents for the units of the rate constant. For most chemists this is simply what we expect from using a dimensional analysis as can be seen from the last example in Table 1.

Taking the last example from Table 1

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2} \quad (7)$$

The left-hand side of the equation has the units [concentration][time]⁻¹ and the right-hand side has the units of $[k] \times [\text{Concentration}]^{3/2}$ so we have

$$[\text{concentration}][\text{time}]^{-1} = [k][\text{concentration}]^{3/2} \quad (8)$$

Showing that for a reaction with order 1.5 the units of the rate constant will be

$$[k] = [\text{concentration}]^{-1/2}[\text{time}]^{-1} \quad (9)$$

In general terms this is a logical consequence of and perfectly consistent with the use of quantity calculus [9].

Rate constants and equilibrium constants

There is also the more often encountered problem with quantities that have dimensions (and units) when we need to take mathematical functions of these quantities, for example the logarithm of the rate constant in applying the Arrhenius equation

$$k = A e^{(-E_a/RT)} \quad (10)$$

or alternatively

$$\ln k = \ln A - \frac{E_a}{RT} \quad (11)$$

This equation is often seen by students as an unusual equation as the units of the Arrhenius A factor, A , are the same as the units of the k , whatever the order of the reaction. While not all rate constants have this temperature dependence, the Arrhenius equation with slight modifications is a very powerful model, particularly in comparison of related chemical reactions. When determining the parameters for the Arrhenius equation from experimental rate constant temperature dependence data, we typically want to plot $\ln k$ vs. $1/T$. We usually present this as taking $\ln(k/\text{units})$ to solve the dilemma of taking a function of units and insist that the axis labels reflect this.

There is a parallel here with chemical thermodynamic equilibrium constants, where the simplest expression of the equilibrium constant in terms of the species concentrations for the reaction,



is

$$K_c = \frac{[\text{P}]}{[\text{A}][\text{B}]} \quad (13)$$

which gives an expression for the equilibrium constant with units. This is not directly compatible with the thermodynamic quantities, from which we derive

$$\Delta G^\ominus = -RT \ln(K^\ominus) \quad (14)$$

as this implies the equilibrium constant, K^\ominus to be dimensionless.

Further if we consider the kinetics of the reversible reaction $A + B = P$ and the principle of detailed balance, then at equilibrium rates of the forward and reverse reactions must be the same (principle of detailed balance),

$$k_f[A][B] = k_r[P] \quad (15)$$

and therefore we have $k_f/k_r = [P]/([A][B])$, which has the units of $[\text{concentration}]^{-1}$ as expected from above but is not the dimensionless thermodynamic equilibrium constant that would be obtained from Eq. (14). This is, for example, an important issue when deriving the thermodynamic form of the Transition State Theory equations [10].

In reality we should use activities for the effective concentrations for the thermodynamic relationships. Some chemists, especially when teaching, take advantage of this and define the activity relative to a standard state concentration, c^\ominus . This then gives,

$$K_{\text{eq}} = \frac{a_P}{a_A a_B} \quad (16)$$

with $a(A) = \gamma[A]/c^\ominus$ where γ is the activity coefficient, and similarly for the other species.

$$\begin{aligned} K_{\text{eq}} &= \frac{\gamma_P}{\gamma_A \gamma_B} \frac{[P]/c^\ominus}{[A]/c^\ominus [B]/c^\ominus} = c^\ominus \frac{\gamma_P}{\gamma_A \gamma_B} \frac{[P]}{[A][B]} \\ &= c^\ominus \frac{\gamma_P}{\gamma_A \gamma_B} K_c \end{aligned} \quad (17)$$

At low concentrations when the solutions are ideal and $\gamma = 1$, we get

$$K_{\text{eq}} = c^\ominus K_c \quad (18)$$

Which gives us a dimensionless equilibrium constant which we can then use in thermodynamic equations as long as we also remember the associate standard state. We could adopt a similar approach in chemical kinetics and define the rate with respect to both a standard state concentration (c^\ominus) and standard time (t^\ominus)

$$\frac{v}{c^\ominus/t^\ominus} = k \left(\frac{[A]}{c^\ominus} \right)^n \left(\frac{[B]}{c^\ominus} \right)^m = k (a_A)^n (a_B)^m \quad (19)$$

Defined in this way the rate constant would have no units and there would be no difference for different reaction orders, or rate laws that are not simple power laws. A unitless rate constant makes the use of logarithms straightforward. The units are not hidden but made explicit in the use of an appropriate standard state concentration.

These approaches solve the problem that initially introduced this discussion and it leads to the rate constant being dimensionless whatever the nature of the rate equation and so there is no need for non-integral powers of the base SI units. It also is simple to take any function of the rate constant.

If we use the activities but leave the rate defined in the usual way, the result will be an inconsistency as the right hand side of the equation (the rate) will have units of concentration per time but the left hand side will have the concentrations scaled out by the division by the standard state concentration. The rate constant would then always have the same units as the rate (concentration per time) but this still leaves the problems with $\ln(k)$ as described above.

Conclusion

The approaches we proposed in this paper have the advantage of greater consistency for the units of reaction rate constants, but we fully acknowledge that the disadvantage is that it is then not possible to infer the order of the reaction from the units of the rate constant. We note that referring quantities to a set of standard values is a general way to generate dimensionless equations and can be quite widely used. In chemistry the relevant standard state values are already key to the discussions of thermodynamics and so are already present in kinetics even if these are not always made explicit in the discussions. Related issues arise when using dimensionless quantities, which are fine from the perspective of mathematical transformation but do not carry important quantity information, for example in the expression of angle (radian and degree) or ratio concentrations.

Our hope is that this discussion will lead to more chemists thinking carefully about the meaning of these basic chemical quantities and the role of standard states, even if it does not lead to a change in the recommended way the chemistry community expresses rate constants.

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