

For Two of the Three Reaction Orders, “Half-Life” Is Not Even a Property of the Substance

— At Zeroth Order Successive Half-Lives Shorten **5.000** → **2.500** → **1.250**; at Second Order They Lengthen **10.000** → **20.000** → **40.000** — Only First Order Holds Still — [Paper 346]

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— *From thinking to syncing.* —

Abstract

“Half-life” is spoken of as a constant attached to a substance. This paper asks when it is a constant—the answer is only when the reaction is first order. No new mathematical theorem and no new law is claimed. First, at zeroth order $t_{1/2}$ is proportional to the initial concentration and at second order inversely so (Section 2). Second, this is the core of the paper. At zeroth and second order the half-life changes from one halving to the next within one sample (Section 3). Third, at zeroth order successive half-lives run **5.000** → **2.500** → **1.250**, halving each time (Section 3). Fourth, at second order they run **10.000** → **20.000** → **40.000**, doubling each time (Section 3). Fifth, only first order stays at **6.931472**. Radioactive decay can be spoken of by half-life because it is first order (Section 3). Sixth, the separator is whether the quantity belongs to the substance or to its present state (Section 5).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed——reaction order, integrated rate laws, and the half-life expressions for zeroth, first and second order are all standard. We settle no mechanism——the chemistry of which reaction takes which order is not entered. Order is taken as given. We do not treat the nucleus——the mechanisms of radioactive decay are not entered. They belong to Paper 283. It is mentioned and no more. We do not treat composite reactions——reversible, consecutive, and pseudo- n th-order reactions are not entered. We do not treat temperature dependence—— k is held fixed; Arrhenius behaviour is not the subject. We do not treat fractional orders——only zeroth, first and second. Relation to earlier papers: Paper 283 showed “half-life” not to be one mechanism, the same “double the Q ” giving 5.69×10^{18} in alpha decay, 32 in beta and 8 in gamma——this paper makes a different claim. All three mechanisms in 283 are exponential decays, where the half-life is a well-defined constant; what differed among them was sensitivity to Q . What this paper says is that at zeroth and second order the half-life is not even a constant: its value changes from one halving to the next within one sample. 283 counts three origins of one quantity; this paper counts the cases in which the quantity does not exist. Paper 240 counted “mass” as seven things——one word naming several, a family this paper joins. Paper 300 showed whether two things share a root is decidable——the three orders have distinct roots from one another by that test. Paper 338 asked whether a promise follows a gap in nature——there a classification was measurable; here “is it a constant” is measurable. What is added is tabulating three successive half-lives to show only first order holds still, giving in numbers the halving at zeroth order and the doubling at second, designing the difference from Paper 283 explicitly, and putting the separator on property against state.

1. Notation and the Question

Setting: Consider a substance of concentration C disappearing. The power of concentration the rate follows is called the reaction order.

Order	Rate law	Half-life $t_{1/2}$
Zeroth	$-dC/dt = k$	$C_0/2k$
First	$-dC/dt = kC$	$\ln 2/k$
Second	$-dC/dt = kC^2$	$1/(kC_0)$

Observation 1.1

In the last column, only first order lacks C_0 . Zeroth has it above and second below——whether the half-life depends on the initial concentration is divided by order.

Observation 1.2

In ordinary speech, “half-life” has first order in mind. Radioactive decay, the elimination of a drug, the discharge of a capacitor—all first order, and so the half-life looks like a number attached to the substance.

Observation 1.3

The way of measuring is fixed first. The rate constant is set to $k = 0.1$ (its units differ by order) and time is in arbitrary units—only ratios are compared, so the choice of units does not affect the conclusion.

Question: When does “half-life” become a property of the substance?

2. Quadruple the Initial Concentration and Zeroth Order Quadruples, Second Order Quarters

Calculation 2.1: Half-lives at three orders against initial concentration (computed in this paper).

Order	$C_0 = 1$	$C_0 = 2$	$C_0 = 4$	Dependence on C_0
Zeroth	5.000	10.000	20.000	proportional
First	6.931	6.931	6.931	none
Second	10.000	5.000	2.500	inverse

Observation 2.2

A check—the first-order 6.931472 equals $\ln 2/k = \ln 2/0.1$. And quadrupling C_0 multiplies zeroth order by exactly 4.0000 and second order by exactly 0.2500—the formulas are confirmed by their ratios before the table is read.

Observation 2.3

Three rows pointing three different ways. Rising, unmoved, falling—one word, “half-life”, behaving in three ways against the initial concentration.

Observation 2.4

At zeroth and second order, “what is the half-life of this substance” cannot be answered. The number is undetermined without a concentration——only at first order can it be answered without one.

Observation 2.5

So far this compares separate experiments at different initial concentrations. Different samples——the next section looks inside a single one.

3. The Core: Within One Sample, the Half-Life Changes Each Time

Setting: Prepare one sample at $C_0 = 1$ and leave it. Time the fall to half, then the fall to half again, then once more.

Calculation 3.1: Three successive half-lives (computed in this paper).

Order	First	Second	Third	Change
Zeroth	5.000	2.500	1.250	halving each time
First	6.931	6.931	6.931	unchanged
Second	10.000	20.000	40.000	doubling each time

Observation 3.2

This is the core of the paper. At zeroth and second order the value of the half-life changes within one sample——the number that the word “half-life” names differs each time it is measured.

Observation 3.3

So in these two, the half-life is not a property of the substance. The same sample, the same substance, the same temperature——only the concentration at that moment changed. It is a function of state, not a property.

Observation 3.4

At zeroth order it goes faster as it proceeds. 5.000, 2.500, 1.250—the rate does not depend on concentration, so the less remains the sooner it is spent. It vanishes completely in finite time.

Observation 3.5

At second order it goes slower as it proceeds. 10.000, 20.000, 40.000—two molecules must meet, so the thinner it becomes the harder that is. It never quite finishes.

Observation 3.6

Only first order gives the same 6.931472 from any starting moment. And this is the defining property of the exponential—“decaying at a constant proportion” and “having a constant half-life” are one statement said twice.

Observation 3.7

Radioactive decay can be spoken of by half-life because it is first order. Nuclei break one at a time, independently, needing no neighbour—had two nuclei needed to meet, the half-life would have lengthened at every measurement.

4. Setting Out the Difference from Paper 283

Setting: Paper 283 also wrote that “half-life” is not one mechanism. What differs here should be made plain.

	Paper 283	This paper
Subject	nuclei (alpha, beta, gamma)	chemical reactions (orders 0, 1, 2)
All three are	exponential decays	not necessarily exponential
The half-life is	a constant in all three	a constant only at first order
What differs is	sensitivity to Q (10^{17})	whether it is a constant at all

Observation 4.1

In the three mechanisms of 283, the half-life is a well-defined constant in every case. Alpha, beta and gamma are all exponential, and the half-life does not change within one sample——what 283 measured was how sensitive that constant is to the released energy.

Observation 4.2

This paper stands one step before that. At zeroth and second order no number exists that could be called the constant——283 counts three origins of one quantity; this paper counts the cases in which the quantity itself does not arise.

Observation 4.3

Together they make a staircase of three steps.

Step	Question	Answered by
First	Is the half-life a constant?	this paper (only at first order)
Second	Granting it is, is there one mechanism?	Paper 283 (three)
Third	How much do the sensitivities differ?	Paper 283 (10^{17})

Observation 4.4

This paper lays a step beneath 283. 283 could compare its three because all three were constants——where there is no constant, there is nothing determinate to compare.

Observation 4.5

To be stated honestly——this paper does not correct 283. Everything 283 claims is about nuclei, and there it is right——this paper works in another domain (chemical kinetics) on another question (is it a constant). Under one word, different steps.

5. The Separator: A Property of the Substance, or of Its Present State?

Observation 5.1

The separator——whether the quantity is attached to the substance or to the concentration of the moment.

	Dependence on C_0	Within one sample	“The half-life of this substance”
Zeroth	proportional	halving	cannot be answered
First	none	constant	can be answered
Second	inverse	doubling	cannot be answered

Observation 5.2

The separator is not on the side of the substance. One substance changes order with the conditions——saturate a catalyst and it becomes zeroth order; dilute and it approaches first. Whether the half-life is a constant is decided by circumstance, not by the substance.

Observation 5.3

And the separator can be measured. Time two successive half-lives in one sample; if the value changes it is not first order——shorter means toward zeroth, longer means toward second. One experiment gives the direction of the order.

Observation 5.4

This is used in practice. For drugs showing zero-order elimination, such as ethanol, the apparent “half-life” is longer at higher blood concentration——set a dose assuming a constant and one errs on the unsafe side.

Observation 5.5

To be stated honestly——real reactions can change order partway.Beginning at zeroth order and moving to first as substrate falls (Michaelis-Menten)——this paper treats each order in pure form and does not take up the transition.

Observation 5.6

One last thing——the word “half-life” sounds like a promise of constancy because it was coined in a first-order setting.It was made for radioactive decay, and there it was right——the word was later carried into other settings, where the promise is not kept.

6. The Census and the Close

1. Zeroth proportional to C_0 , second inverse (Calculation 2.1): **only first is free of it.**
2. Quadruple C_0 : 4.0000 and 0.2500 (Observation 2.2): **the formulas check.**
3. Zeroth runs 5.000 $\rightarrow$ 2.500 $\rightarrow$ 1.250 (Calculation 3.1): **halving each time.**
4. Second runs 10.000 $\rightarrow$ 20.000 $\rightarrow$ 40.000 (Calculation 3.1): **doubling each time.**
5. **Only first stays at 6.931472** (Calculation 3.1): **from any starting moment.**
6. **Zeroth vanishes in finite time** (Observation 3.4): **the less remains the sooner.**
7. **Second never quite finishes** (Observation 3.5): **the thinner, the harder to meet.**
8. **All three of 283 are constants** (Observation 4.1): **this paper asks one step earlier.**
9. **Two successive half-lives give the order’s direction** (Observation 5.3): **the separator is measurable.**
10. **The word was coined at first order** (Observation 5.6): **carried elsewhere, the promise fails.**

Closing: “Half-life” is spoken of as a constant attached to a substance, and it is a constant only when the reaction is first order——at zeroth order $t_{1/2} = C_0/2k$ is proportional to the initial concentration and at second order $t_{1/2} = 1/(kC_0)$ is inversely so. Only first order is free of C_0 .And the core is not about comparing separate samples——within one sample the value of the half-life changes from one halving to the next. At zeroth order successive half-lives run 5.000 $\rightarrow$ 2.500 $\rightarrow$ 1.250, halving each time; at second order 10.000 $\rightarrow$ 20.000 $\rightarrow$ 40.000, doubling each time. Only first order stays at 6.931472.So in these two the half-life is not a property of the substance——the same sample, substance and temperature, with only the concentration of the moment changed. It is a function of state, not a property. At zeroth order the rate does not depend on concentration, so the less remains the

sooner it is spent and it vanishes in finite time; at second order two molecules must meet, so the thinner it becomes the slower it goes and it never quite finishes. Radioactive decay can be spoken of by half-life because it is first order——nuclei break one at a time, needing no neighbour. Had two nuclei needed to meet, the half-life would have lengthened at every measurement. The difference from Paper 283, set out plainly——283 wrote that “half-life” is not one mechanism and that the same “double the Q ” gives 5.69×10^{18} in alpha decay, 32 in beta and 8 in gamma. But all three of its mechanisms are exponential decays, where the half-life is a well-defined constant. 283 measured the sensitivity of that constant; this paper stands one step earlier, where at zeroth and second order no number exists that could be called the constant. 283 could compare its three because all three were constants. One thing separates them——whether the quantity is attached to the substance or to the concentration of the moment. The separator is not on the side of the substance——saturate a catalyst and one substance becomes zeroth order, dilute it and it approaches first; circumstance decides, not the substance. And it can be measured——time two successive half-lives in one sample: shorter means toward zeroth, longer means toward second. To be said honestly——this paper does not correct 283. Everything 283 claims is about nuclei and there it is right; this works in another domain on another question. Real reactions can also change order partway, and each order is treated here in pure form. One last thing——the word “half-life” sounds like a promise of constancy because it was coined in a first-order setting. It was made for radioactive decay, and there it was right. The word was later carried into other settings, where the promise is not kept.

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