Strengthening Students' Math Fluencies through Calculator-Free Chemistry Calculations

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Abstract

In a previous study of students in second-semester general chemistry classes at the University of Minnesota, higher scores on a calculator-free Math Assessment, administered at the start of the semester, were found to correlate with higher grades in this course, despite the use of calculators during exams.[1] The present paper describes some methods subsequently used to enhance students' math fluency through solving numerical problems using pencil-and-paper math, without the use of a calculator. When doing such problems in class, the instructor can efficiently interleave reminders of basic algebraic methods to simplify expressions, to work with common and natural logs, and to estimate results to one or two significant figures. Multiple-choice exams incorporating problems of this type, in which calculators were not allowed, were also administered. It is hoped that these methods can help motivate students to gain greater intuitive and conceptual insight through solving quantitative chemistry problems, and to become more fluent in expressing science in the language of math. Examples of such problems and their pencil-and-paper solution methods are presented in the areas of chemical equilibrium, acid-base reactions, buffers and titrations. Students' evaluations of this pedagogical approach are also discussed. Finally, we discuss some "broader impacts" of strengthening basic math skills, using as an example a suggested connection between some eligible voters' understanding of percentages and probabilities, and the outcome of the 2016 presidential election.

I. Introduction

Nearly a decade ago, we reported a study of the math fluencies of second-semester general chemistry students at the University of Minnesota (Twin Cities), based on a Math Assessment for which calculators were not allowed.[1] Although these scores did not count toward the course grades, and calculators were allowed on all exams (and in the labs), students' scores on this calculator-free Math Assessment were found to correlate with their final course grades. This Math Assessment and its answer key are included in the Supplemental Material for that paper.[1] The slightly modified version that we currently use (23 multiple-choice questions, 40 minutes) can be viewed and downloaded here:

> ay17.moodle.umn.edu
> Title: Math Fluency in General Chemistry
> login internetID: mathchem
> password: No-calculators

In addition to the 38 multiple-choice problems on chemical equilibrium and acid-base chemistry included in the Appendix to the present paper, a document titled "Multiple-Choice Numerical Problems from Old Exams with Answers Describing Calculator-Free Solution Methods" is posted (136 pages). This packet has 165 problems on all of the quantitative topics that we typically cover in our second-semester general chemistry class, including the properties of solutions, kinetics, chemical equilibrium, acid-base reactions, ionic equilibria, entropy and free energy, and electrochemistry (e.g., Chapters 13 and 16-21 in Silberberg's "Chemistry").

Also posted is a document titled "Math Review for Calculator-Free Problem Solving" (30 pages), which can help second semester chemistry students review their high school (pre-calculus) math. In addition, math problems based on the chemistry problems in "Multiple-Choice Numerical Problems", with the chemistry content removed, are provided in a separate document titled "Math Practice Problems for Calculator-Free Numerical Problem Solving" (50 pages). This resource can be helpful for students who want to brush up on useful math techniques before starting the chemistry class.

Readers are welcome to view and download all of the posted materials, to use them as is, or to modify them as needed, for use in their high school and college chemistry (and math) classes. Please let the author know of any errors spotted, so that they can be corrected (dleopold@umn.edu).

Participants in this conference are probably amply convinced of the importance of improving the math fluencies of our chemistry students at both the high school and college levels, and are familiar with some of the rich literature on this subject. For example, one of our conference organizers, Rick Nelson, and his collaborator, JudithAnn Hartman, have recently published an extensive study entitled, "Automaticity in Computation and Student Success in Introductory Physical Science Courses" (August 2016), which can be downloaded from the ArXiv site.[2] As these authors conclude,

> "In physical science courses, is it important that students be able to solve fundamental mathematical calculations without reliance on computers or calculators?" We found that science says yes. "Arithmetic facts and fundamental algorithms" must be "thoroughly mastered, and indeed, overlearned" to avoid the bottleneck in novel working memory. (Ref. 2, p. 20)

Section II describes some of the methods we have used to help our second-semester general chemistry college students improve their math fluency, and hopefully to extract a deeper conceptual understanding from the many numerical problems that they solve in this course. These include the following:

- **A.** Solving numerical problems in class and on homework without a calculator
- **B.** Reminding students of pencil-and-paper math methods and providing practice problems
- **C.** Giving at least one calculator-free chemistry exam with questions requiring calculations
- **D.** Accommodating students who suffer from severe math anxiety or discalculia

In Section IIA, examples are taken from 8 of the 38 problems involving chemical equilibria and acid-base reactions which are included in the Appendix to this paper.

Section III presents some of the student feedback concerning our "experiment" in giving calculator-free quantitative exams. In **Section IV**, some possible broader impacts of enhancing the math fluencies of our high school and college chemistry students are discussed.

II. Methods to Encourage General Chemistry Students to Improve their Math Fluency

IIA. Solving numerical problems in class and in homework without a calculator

As an example, consider the calculations of pH values in acid-base chemistry, which comprise a substantial portion (2 chapters out of 8) of our second-semester general chemistry class. To test students' understanding of the meaning of common, base-10 logs at the start of the semester, two questions on our calculator-free Math Assessment are the following. So that the students do not think that we mean the natural log, these are immediately preceded by the prominent note:

==========

In the following questions:

a, b, c, d are numbers

log means <u>common</u> logarithm (base 10, that is, $\log_{10}$)

ln means <u>natural</u> logarithm (base e = 2.71828..., that is, $\log_e$)

1. What is the log of 100?

A.	10	F.	-1
B.	3	G.	-2
C.	2	H.	-3
D.	1	I.	-4
E.	0	J.	none of the above (A-I)

Answer: C. 2

2. What is the log of 0.0001 ?

A.	4	F.	-1
B.	3	G.	-2
C.	2	H.	-3
D.	1	I.	-4
E.	0.01	J.	none of the above (A-I)

Answer: I. -4

==========

We last gave this calculator-free Math Assessment at the start of the Spring 2016 semester to a class of 139 students in our second-semester general chemistry class (Chem 1062, "Chemical Principles II"). For the first question, 55% of the students answered correctly that log (100) = 2, while 36% chose 10. Thus, about one-third of the class apparently confused the log with the square root.

This inference is supported by the students' responses to the second question, for which 50% correctly chose log (0.0001) = -4. Again, the most popular incorrect answer (chosen by 21% of the students) was the square root, 0.01.

Since it is likely that essentially all of our students knew that $10^2 = 100$ and $10^{-4} = 0.0001$, it appears that only about half remembered the *meaning* of the common log as the exponent of 10.

Results of this type are apparently not limited to our U of M general chemistry students. A 2006 paper concerning Australian students in biochemistry and biological chemistry courses had the memorable title, "Student Understanding of pH: "I Don't Know What the Log Actually Is, I Only Know Where the Button Is On My Calculator".[3]

Our results for Spring 2016 were somewhat improved over those obtained at the start of the corresponding chemistry class (then numbered Chem 1022) a decade earlier, in Spring 2006.[1] At that time, 50% of the 360 students correctly chose log (100) = 2 and 44% chose 10 (as compared with 55% and 36%, respectively, in 2016). In 2006, 41% of the students correctly chose -4 for log (0.0001), while 27% chose 0.01 (as compared with 50% and 21% in 2016, respectively). However, it goes without saying that it would have been better for <u>all</u> of the students to have correctly answered these very simple questions.

In the intervening decade, our admissions criteria at the U of M have become increasingly selective,[4] and high school requirements now include 4 years of math and 3 years of science.[5] Minnesotans comprised 66% of the 29,000 undergraduates on our U of M Twin Cities campus, as of Spring 2016.[6] New Minnesota Mathematics Standards and Benchmarks for Grades K-12 were introduced in 2007.[7,8] Changes included the requirements to complete Algebra I by the end of 8th grade, as well as an additional 3 years of math, including Algebra II, in high school.[8] Interestingly, it was pointed out that "...logarithms are usually introduced in algebra II, but mastery of the fundamentals of logarithms is not expected until precalculus or college algebra. For this reason, logarithms are not mentioned in the 9-11th grade standards and benchmarks." [8]

With this insight into the math backgrounds that a significant percentage of our students bring to their college chemistry classes, we decided to interleave more basic math review and "mental math" into lectures and active learning exercises. In addition, during four semesters, in which we had the flexibility to allow all students to take twice the usual time for exams, we did not allow the use of calculators on our second midterm exam. This exam, which did count toward the students' course grades, covered chemical equilibrium and acid-base chemistry, including buffers and titrations. As noted in the Introduction, 38 multiple-choice, quantitative questions selected from these four exams, with explanations of the pencil-and-paper methods that may be used to solve them without a calculator, are included in the Appendix to this paper, and 8 of them are used as examples in the following discussion.

Sample problems:

In class discussions, when introducing pH calculations, one can start with simple problems that allow a review of base-10 logarithms to be interleaved, without taking much class time away from the chemistry. It is helpful to refer to the results of the Math Assessment for that class, so that students who know this material realize that there are others in the class for whom this review is useful.

When introducing pH calculations of a solution of a strong acid, one might start with a problem like the following (like #18 in the Appendix).

==========

• ***What is the pH of a 0.001 M aqueous solution of nitric acid (HNO_3) ?***

Answer: 3.0

==========

This is like the second question discussed above from the Math Assessment (log 0.0001 = -4), but here we have included the correct number of significant figures in the pH (one).

After inviting students to solve this problem "in their heads", one can quickly review the meaning of the common, base-10 log as the exponent of 10. A few examples, such as those listed below, can remind students of what they really already know, to help them more readily access this knowledge in the future.

$10 = 10^1$	so the log of 10 is 1	log (10) = 1
$100 = 10 \times 10 = 10^2$	log of 100 is 2	log (100) = 2
$1{,}000 = 10 \times 10 \times 10 = 10^3$	log of 1,000 is 3	log (1,000) = 3
$\mathbf{10^0 = 1}$	**log of 1 is 0**	**log (1) = 0**
$0.1 = 1/10 = 10^{-1}$	log of 0.1 is -1	log (0.1) = -1
$0.01 = 1/100 = 10^{-2}$	log of 0.01 is -2	log (0.01) = -2
$0.001 = 1/1{,}000 = 10^{-3}$	log of 0.001 is -3	log (0.001) = -3

One might also point out that $\mathbf{10^0 = 1}$ is required by the relationship:

$10^a \times 10^b = 10^{a+b}$ **When we <u>multiply</u> the numbers, we <u>add</u> the exponents**

For example,

$10^2 \times 10^0 = 10^{2+0} = 10^2$

$10^3 \times 10^0 = 10^{3+0} = 10^3$

Since any number multiplied by 10^0 remains unchanged, 10^0 must be exactly 1 (as is true for all bases, not just for base 10).

Also, one can remind the students that the same relationship ($10^a \times 10^b = 10^{a+b}$) tells us what **negative exponents** mean:

For example,

$10^2 \times 10^{-2} = 10^{(2-2)} = 10^0 = 1$

So, 10^{-2} must mean 1/100, the reciprocal (or inverse) of 10^2.

In general (as is true for any base, not just for 10):

$10^{-a} = 1 / 10^a$ **When the number is inverted, the exponent (log) changes sign**

We can also use this relationship ($10^a \times 10^b = 10^{a+b}$) to remind the students of the meaning of **fractional exponents**.

For example,

$10^{½} \times 10^{½} = 10^{(½ + ½)} = 10^1 = 10$

Since both numbers being multiplied together are identical and the product is 10, each must be $\sqrt{10}$.

Similarly,

$10^{1/3} \times 10^{1/3} \times 10^{1/3} = 10^{(1/3 + 1/3 + 1/3)} = 10^1 = 10$

Since multiplying these 3 identical numbers together gives 10, $10^{1/3}$ must mean the cube root of 10.

Regarding significant figures, one can remind the students that the number of digits after (to the right of) the decimal point in the log (or in the pH) count as significant figures (with the number before the decimal point representing the order of magnitude). Thus, the number of digits after the decimal point in the pH should be equal to the number of sig figs in the concentration of H_3O^+. In this problem, the concentration of 0.001 M is given to 1 sig fig, so we write the log as -3.0 (and the pH as 3.0), with one digit after the decimal point.

The next problem (#19 in the Appendix) requires calculating the pH of a strong acid whose concentration is not exactly a negative power of 10.

==========

- ***What is the pH of a 5×10^{-2} M $HClO_4$ (perchloric acid) solution?***

Answer: 1.3

==========

Here, we can use the relationship:

log (m n) = log (m) + log (n) ***The log of the product is the sum of the logs.***

For example, let m = 100 and n = 1,000

log of product: log (100 × 1000) = log (100,000) = log (10^5) = 5

sum of logs: log (100) + log (1,000) = log (10^2) + log (10^3) = 2 + 3 = 5

As another example, let m = 10 and n = 0.10:

log of product: log (10 × 0.10) = log (1) = log (10^0) = 0

sum of logs: log (10) + log (0.10) = log (10^1) + log (10^{-1}) = 1 - 1 = 0

This relationship (log (m n) = log (m) + log (n)) is equivalent to the one discussed above:

$10^a \times 10^b = 10^{a+b}$.

To show this, we can take the logs of both sides, and we still have an equality:

log ($10^a \times 10^b$) = log (10^{a+b})

Since the log is the number you have to raise 10 to, to get the number you're taking the log of, on the right hand side, we have:

$$\log (10^{a+b}) = a + b,$$

Substituting, we have:

$$\log (10^a \times 10^b) = \log (10^{a+b}) = a + b$$

Setting $m = 10^a$ (so $a = \log m$) and $n = 10^b$ (so $b = \log n$), we have:

$$\log (m\, n) = \log m + \log n$$

Thus, we have shown that "the log of the product of two (or more) numbers is the sum of their logs".

In our 2016 Math Assessment, 65% of the students correctly answered the question, "What is: log (a b)?" with "log a + log b", and 25% incorrectly chose the product, (log a)(log b). These results were about the same as those obtained in 2006 (64% and 27%, respectively).

The following poem, summarizing some of these logarithmic relationships, was written by Mrs. Deedee Stacy, her 4th grade students at Mounds Park Academy in Maplewood, Minnesota, and the author, after we held a few classes on this interesting topic in 2007. These eager 9 or 10 year old students, who had just learned about exponents and powers of 10, were delighted to learn to do calculations "in their heads" for which many college students required a calculator!

The Common Log

You know ten squared's one hundred
The log of that is two.
Just look at Mr. Exponent
That's all you have to do.

Ten to the ninth's one billion
The log of that is nine.
Just use the little exponent
And you will do just fine.

A hundred times ten's a thousand
And two plus one is three.
If we multiply the numbers
The logs add, naturally.

So the log of one is zero,
And now we can divine
If a number is inverted
Its log just changes sign.

Getting back to our pH problem, we needed to calculate the log of 5×10^{-2} .

The relation discussed above (log (m n) = log m + log n) applies even if m and n are *not* integer powers of 10). So, setting m = 5 and n = 1×10^{-2} , we can write this as:

$\log (5 \times 10^{-2}) = \log 5 + \log (1 \times 10^{-2}) = \log 5 - 2.0$

What is the log of 5?

We know log (5) must be less than log (10), which is 1.

It must also be greater than log (1), which is 0.

So, log (5) must be between 0 and 1. Actually, to 2 sig figs, it's 0.70 .

Here is a table of logs (rounded to 2 sig figs) of integers up to 10, which is included with all of our exams, is on p. 4 of the Appendix, and is handy to use when doing homework problems:

$\log 1 = 0.$	$\log 2 \approx 0.30$	$\log 3 \approx 0.48$	$\log 4 \approx 0.60$	$\log 5 \approx 0.70$
$\log 6 \approx 0.78$	$\log 7 \approx 0.85$	$\log 8 \approx 0.90$	$\log 9 \approx 0.95$	$\log 10 = 1.$

One can quickly point out to the students that these values are consistent with the relationship:

log (m n) = log m + log n

For example,

$\log (4) = \log (2 \times 2) = \log 2 + \log 2 = 0.30 + 0.30 = 0.60$

$\log (6) = \log (2 \times 3) = \log 2 + \log 3 = 0.30 + 0.48 = 0.78$

$\log (8) = \log (2 \times 4) = \log (2 \times 2 \times 2) = 0.30 + 0.30 + 0.30 = 0.90$

$\log (9) = \log (3 \times 3) = \log 3 + \log 3 = 0.48 + 0.48 = 0.96$ (actually it's 0.954, so is closer to 0.95)

So, one can just remember the logs of four integers, and easily deduce the others.

To just one sig fig, these are:

$\log 2 \approx 0.3$	$\log 3 \approx 0.5$	$\log 5 \approx 0.7$	$\log 7 \approx 0.8$

Going back to the pH problem, since log 5 = 0.7, we have

$$\log (5 \text{ x } 10^{-2}) = \log 5 + \log (1 \text{ x } 10^{-2}) = 0.7 - 2.0 = -1.3$$

Since the pH is -1 times the log, the pH is +1.3 .

Next, one can introduce the opposite type of problem: given the pH, solve for the concentration of [OH^-] (like #22 in the Appendix):

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• **$Ca(OH)_2$ is dissolved in water at room temperature until the pH of the solution is 10.7 . What is the hydroxide ion concentration, [OH^-], in the solution ?**

Answer: 5×10^{-4} M

==========

In this problem, we need to go from the pH to the concentration of [OH^-]. (It is not necessary to know that the source of the hydroxide anion is $Ca(OH)_2$.)

One can point out to the students that one way to do this is to first obtain the pOH:

$$pOH = 14.0 - pH = 14.0 - 10.7 = 3.3 = -\log [OH^-]$$

Thus, $[OH^-] = 10^{-pOH} = 10^{-3.3}$

How can we calculate the value of a number with a non-integral, negative exponent?
An easy way to do this is to express the exponent as the sum of a negative integer and a positive decimal:

$$-3.3 = 0.7 - 4.0$$

Then, we can use the relationship discussed above - when we multiply two numbers, we add their exponents:

$$10^{a+b} = 10^a \times 10^b$$

So, setting a = +0.7 and b = -4,
$$10^{-3.3} = 10^{+0.7} \times 10^{-4}$$

We already know that the log of 5 is 0.7, which is the same as saying that $10^{0.7} = 5$, so:
$$[OH^-] = 10^{-pOH} = 10^{-3.3} = 10^{+0.7} \times 10^{-4} = 5 \text{ x } 10^{-4} \text{ M.}$$

These types of calculations can also be extended to buffer problems using the Henderson-Hasselbalch equation. For example (#31 in the Appendix):

==========

• Calculate the pH of a 5 L solution containing 0.3 mol of cyanic acid (HCNO, $K_a = 2 \times 10^{-4}$) and 0.6 mol of sodium cyanate (NaCNO).

Answer: 4.0

==========

This is a buffer solution, so we can use the Henderson-Hasselbalch (HH) equation:

$pH \approx pK_a + \log ([base]_o/[acid]_o)$

(where $[acid]_o$ and $[base]_o$ are the initial concentrations of the weak acid, HCNO, and its conjugate weak base, CNO^-, prior to their reactions with water).

$pK_a = -\log (2 \times 10^{-4}) = - (\log 2 + \log(1\times10^{-4})) = -(0.3 - 4.0) = - (-3.7) = 3.7$

$pH = 3.7 + \log (0.6 / 0.3) = 3.7 + \log 2 = 3.7 + 0.3 = 4.0$

(where log 2 = 0.3, discussed above, is provided on the equation sheet)

(Since the HH equation involves a ratio of concentrations of the base to acid in the same volume of solution, the volumes cancel in the numerator and denominator, so we can use the ratio of moles and avoid the extra step of converting to concentrations.)

The following buffer problem can be solved using the same methods (#32 in the Appendix):

==========

• If 0.025 mole of NaOH is added to 500. mL of a 0.200 M solution of HCN (hydrocyanic acid, pK_a = 9.2), what is the pH of the resulting solution?

Answer: 8.7

==========

Here, the amount of HCN present initially is: (0.50 L)(0.20 mole/L) = 0.10 mole

The reaction of OH^- (from the dissolution of the NaOH) with the acid will go to completion:

	OH^-	+ HCN →	H_2O + CN^- (cyanide ion)
initial	0.025 mole	0.100 mole	0
change	-0.025	-0.025	+0.025
final	≈ 0	0.075	0.025

This is now a buffer solution (since it has similar amounts of a weak acid and its conjugate weak base, and no excess OH^- from the NaOH added).

So, we can use the Henderson-Hasselbalch equation:

$pH = pK_a + \log([base]/[acid])$

$pH = 9.2 + \log(0.025/0.075) = 9.2 + \log(1/3) = 9.2 - \log 3 = 9.2 - 0.5 = 8.7$

Here, to calculate the log of 1/3, we have used

$\log(1/3) = -\log 3$

This follows from:

$\log(m/n) = \log(m) - \log(n)$ ***The log of the ratio is the difference of the logs.***

So, $\log(1/3) = \log 1 - \log 3 = 0 - \log 3 = -\log 3$

This relationship (log (m / n) = log m - log n) can be deduced from the relation

$10^a \times 10^b = 10^{a+b}$

and the meaning of negative exponents ($10^{-b} = 1 / 10^b$), both discussed above.

Thus, $10^a \times 10^{-b} = 10^{a-b} = 10^a \times (1/10^b) = 10^a / 10^b$.

So we have: $10^a / 10^b = 10^{a-b}$

Taking the logs of both sides,

$\log (10^a / 10^b) = \log (10^{(a-b)})$

Since the right hand side is just *a* – *b*,

$\log (10^a / 10^b) = a - b$

Again, substituting m and n, where $m = 10^a$, so log m = a

and $n = 10^b$, so log n = b, we can write:

log (m / n) = log m – log n

Thus, we have shown that "the log of a ratio of two numbers (m/n) is the difference of their logs" (that is, the log of the numerator minus the log of the denominator).

In doing pH problems involving weak acids or weak bases, it is helpful for the student to be able to take square roots of numbers in scientific notation. Here is an example (#26 in the Appendix):

==========

• **Calculate the pH of a 0.3 M solution of benzoic acid (C_6H_5COOH), assuming a K_a value of 6×10^{-5}.**

Answer: 2.4

==========

The reaction is: $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

initial	0.3 M	0	~0
change	-x	x	x
equilibrium	0.3 -x	x	x

$K_a = 6\times10^{-5} \approx x^2 / 0.3$ (since K_a is small)

$x^2 = (6\times10^{-5})(0.3) = 1.8\times10^{-5}$

$x = [H_3O^+] = (1.8\times10^{-5})^{½} = (18 \times 10^{-6})^{½} \approx 4\times10^{-3}$ (since $\sqrt{16} = 4$, and 18 is close to 16)

$pH = -\log [H_3O^+] = -\log (4\times10^{-3}) = -(\log 4 - 3.0) = -(0.6 - 3.0) = -(-2.4) = 2.4$

Here, to calculate the square root, we have used the relationship:

$(10^a)^b = 10^{a \times b}$ When we raise a power of 10 to an exponent, we multiply the exponents.

This is true for other bases as well, not just for 10.

For example, consider: $(10^2)^3$

Cubing a number means to multiply it by itself 3 times, so

$(10^2)^3 = 10^2 \times 10^2 \times 10^2$

Now we can also write each factor of 10^2 as 10×10, giving:

$(10^2)^3 = 10^2 \times 10^2 \times 10^2 = (10 \times 10) \times (10 \times 10) \times (10 \times 10) = 10^{2\times3} = 10^6$

As another example, $(10^{½})^2 = 10^{½} \times 10^{½} = 10^{½ \times 2} = 10^1 = 10$

Again, we see that an exponent of ½ means to take the square root, as was noted above.

Now back to our weak acid problem, where we needed to take the square root of 1.8×10^{-5}.

An easy way to take the square root of a number in scientific notation is to convert it to one with an even exponent:

$$1.8\times10^{-5} = 18 \times 10^{-6}$$

Multiplying the square root of the coefficient (18) by the square root of the exponential term (10^{-6}), and using the relation $(10^a)^b = 10^{a\times b}$, we can write:

$$(18 \times 10^{-6})^{½} = 18^{½} \times (10^{-6})^{½} = 18^{½} \times 10^{-6 \times 1/2} = 18^{½} \times 10^{-3}$$

We can estimate $18^{½}$ (which means $\sqrt{18}$) to be about 4, since 18 is close to 16 and $\sqrt{16} = 4$.

Thus, we have for our pH problem: $x = [H_3O^+] \approx 4\times10^{-3}$

Similarly, to take the cube root of a number in scientific notation, it is convenient to convert it to an expression with an exponent that is divisible by 3. For example (as in problem #13):

$$(1.00\times10^{-12})^{1/3} = 1.00^{1/3} \times (10^{-12})^{1/3} = 1.00 \times 10^{-12/3} = 1.00\times10^{-4}$$

This "trick" for calculating the square or cube roots of numbers in scientific notation is quite handy, and is used in 10 of the 38 problems listed in the Appendix (# 4, 11-13, 15, 23-26, 29).

When doing chemistry problems, it is often necessary to simplify products and ratios of numbers in scientific notation. An example is the following (# 27 in the Appendix):

==========

• **Given that the pH of a 0.02 M solution of a weak monoprotic acid is 5.0, estimate the acid-dissociation constant (K_a) for this acid.**

Answer: 5×10^{-9}

==========

	HA + H_2O	$\rightleftharpoons$	H_3O^+	+ A^-
Equilibrium	$2\times10^{-2} - x$		x	x

$x = [H_3O^+] = 10^{-pH} = 10^{-5.0} = 1 \times 10^{-5}$

Here we can use the small-x approximation, since $2\times10^{-2} - x = 2\times10^{-2} - 1\times10^{-5} = 2\times10^{-2}$ (to 1 sig fig):

$K_a = x^2 / 0.02 = (1\times10^{-5})^2 / (2\times10^{-2}) = (1\times10^{-10}) / (2\times10^{-2}) = 0.5\times10^{-8} = 5\times10^{-9}$

Here, we have used $(10^a)^b = 10^{a\times b}$, discussed above, to obtain
$(1\times10^{-5})^2 = 1^2 \times 10^{-5 \times 2} = 1\times10^{-10}$

We have also used
$(1\times10^{-10}) / (2\times10^{-2}) = (1/2) \times 10^{-10 - (-2)} = 0.5\times10^{-8}$
and then we have converted to standard scientific notation:
$0.5\times10^{-8} = 5 \times10^{-9}$

For many students, reminders of how to multiply and divide numbers in scientific notation can be helpful. As discussed in our Math Review document (Section I J):

• To <u>multiply</u> numbers written in scientific or other exponential notation, e.g.:

$(3.0 \times 10^4)\ (6.0 \times 10^2) = (3.0 \times 6.0) \times 10^{(4 + 2)} = 18 \times 10^6 = 1.8 \times 10^7$

- multiply the coefficients ($3.0 \times 6.0 = 18$)
- add the exponents ($4 + 2 = 6$), i.e., $10^4\times10^2 = 10^6$,
  which means $10{,}000\times100 = 1{,}000{,}000$;
  see Section II B of the Math Review for a discussion of why this works.
- if needed, express the result in standard scientific notation
  (so 18×10^6 becomes 1.8×10^7)

• To <u>divide</u> numbers written in scientific or other exponential notation, e.g.:

$(3.0 \times 10^4) / (6.0 \times 10^2) = (3.0 / 6.0) \times 10^{(4-2)} = 0.50 \times 10^2 = 5.0 \times 10^1$

- divide the coefficients (3.0 / 6.0 = 0.50)
- subtract the exponent in the denominator from the exponent in the numerator

  $10^4 / 10^2 = 10^{(4-2)} = 10^2$ (which means: 10,000 / 100 = 100).

  See Section II E of the Math Review for a further discussion of why this works.
- if needed, express the result in standard scientific notation

  (so 0.50×10^2 becomes 5.0×10^1, which is 50)

Natural logs: Once students are comfortable with working with common logs, it is straightforward to do pencil-and-paper calculations involving natural logs, using relationships such as:

$$\ln a = \ln(10) \log a \approx 2.30 \log a$$

As noted in our Math Review (Section II O), to estimate the natural log of any positive number, *a*, to about ±0.2:

1. Write the number in scientific notation: $m = c \times 10^a$
2. Obtain the common log by adding the log of the coefficient to the exponent:

   $\log m = \log c + a$ (See Section II J)
3. Multiply the common log by 2.3, since $\ln 10 \approx 2.30$, to obtain $\ln a$:

   $\ln m \approx 2.30 \log m$

Example: What is $\ln(3.0 \times 10^{-8})$?

$\log(3.0 \times 10^{-8}) = \log 3.0 + \log 10^{-8} = 0.48 - 8 = -7.52$

$\ln(3.0 \times 10^{-8}) \approx -7.52 \times 2.3 \approx -7.5 \times 2.3 = -17.25$ (exact answer to 2 sig figs = -17.32)

These relationships between common and natural logs can be useful in calculations involving the van't Hoff equation, as well as in other thermodynamics calculations, and in first order kinetics and Arrhenius problems. An example of a problem involving the van't Hoff equation is the following (#14 in the Appendix):

==========

- **Given: $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$**

If the equilibrium constant for this reaction is

1.0×10^{-16} atm^2 at 25 ^oC, and it is 0.10 atm^2 at 325 ^oC,

then the value of ΔH^o (in kJ/mol) is (choose the closest answer):

Answer: 170

==========

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

We can approximate $T_1 = 25^o$ C + 273 ≈ 300 K, $T_2 = 325^o$ C + 273 ≈ 600 K

Since the equilibrium constant <u>increases</u> with increasing temperature, we know that the reaction is endothermic, so ΔH^o is <u>positive</u>.

$$\left(\frac{T_2 - T_1}{T_1 T_2}\right) = \left(\frac{600 - 300}{600\,(300)}\right) = \left(\frac{300}{180{,}000}\right) = \left(\frac{3}{1{,}800}\right) = \left(\frac{1}{600}\right)$$

$K_2 / K_1 = 0.1 / (1\times10^{-16}) = 1\times10^{-1} / (1\times10^{-16}) = 1\times10^{15}$

$\log (K_2 / K_1) = \log (1 \times 10^{15}) = 15$

$\ln (K_2 / K_1) = 2.3 \log (K_2 / K_1) = 2.3\ (15) \approx 35$

Rearranging and approximating R as 8 J/(K•mol):

$$\Delta H^o = \frac{R\ \ln \frac{K_2}{K_1}}{\left(\frac{T_2 - T_1}{T_1 T_2}\right)} = \frac{8(35)}{\left(\frac{1}{600}\right)} = 8(35)(600) = 168{,}000 \approx 170{,}000\ J = 170\ kJ$$

Another benefit of using the sorts of numerical problems in the Appendix is that the simple numbers chosen allow the chemistry concepts to be communicated more clearly. Thus, these types of problems are useful for introducing problems in lectures. The deliberate choice of pencil-and-paper math-friendly numerical values, and estimating results to one or two significant figures, can reduce the extent to which the chemistry is obscured by the math. Of course, in labs, the need for more accurate and precise values often require the use of calculators and/or computational programs.

IIB. Reminding Students of Paper-and-Pencil Math Methods and Providing Math Practice Problems

Since many students come to our second-semester general chemistry classes with an overdependence on calculators, and they no longer have their pre-college math books and worksheets, it is useful to provide review materials. As noted above, readers are welcome to make use of our 30-page "Math Review for Calculator-Free Problem Solving," which can be viewed and downloaded from the Moodle link on p. 1, either using it as is or making their own modifications. Its table of contents is given on the next page. This document attempts to be comprehensive in reviewing the basics and explaining math relationships that students in general chemistry may find useful. (There is even a section on long division, which some students have admitted they were never taught!) This review also includes many sample calculations, to give students a better understanding of how these equations can be used.

During some semesters, we have also provided the option for students who desired extra math review to attend workshops or problem-solving sessions ("ChemFoundations") led by undergraduate, graduate student or postdoctoral volunteers.

Many students have also used online tutorials that they have found to be very useful for math review, including those provided by the Khan Academy: https://www.khanacademy.org/math/ Some additional math resources are listed on p. 17 of our Math Assessment answer key, which is also available at the Moodle site described on p. 1.

By administering the calculator-free Math Assessment during the first week of classes and encouraging students who got low scores to review their high school math to do well in this class, students can be encouraged to make effective use of these resources to help strengthen their math fluency throughout the semester.

Math Review for Calculator-Free Problem Solving

I. Algebra and Scientific Notation **Page(s)**

II. Logarithms and Exponents

IIC. Giving at Least One Calculator-Free Chemistry Exam with Quantitative Questions

As pointed out by Hartman and Nelson and quoted above, "Arithmetic facts and fundamental algorithms" must be "thoroughly mastered, and indeed, overlearned" to avoid the bottleneck in novel working memory." [2] We have found that the best way to motivate students to really master the basic math techniques outlined here is to give at least one midterm exam that counts toward the course grade, including many numerical problems, for which the use of calculators is not permitted. We have done this during four semesters for our Exam 2, typically given during the 9th week. This exam covers chemical equilibrium and acid-base reactions, including buffers and titrations. By then, students have had ample time to brush up on their calculator-free problem solving, and will already have done many such problems in class and for homework.

Our midterm exams each include 20 multiple-choice questions, each graded as 0 or 5 points. Scratch work is not counted, no partial credit is given, and there is no penalty for incorrect answers. Roughly 2/3 of the questions on the second midterm exam typically require calculations for which most students would normally use a calculator. To enable students to do these calculations on paper, we use paper-and-pencil math-friendly numerical values in the problems, and allowed twice the usual time do to the exam (2 hours instead of the usual 1 hour).

The equation sheet provided with the exams also included the following information about the math to help students perform these calculations:

$\sqrt{2} \approx 1.4$, $\sqrt{3} \approx 1.7$, $\sqrt{5} \approx 2.2$, $\sqrt{6} \approx 2.4$, $\sqrt{7} \approx 2.6$, $\sqrt{8} \approx 2.8$ [logs: we use "*ln*" for base *e* and "*log*" for base 10.]

$\log(a \bullet b) = \log(a) + \log(b)$; $\log(a/b) = \log(a) - \log(b)$; $\log(a^n) = n\log(a)$ ←same three relations hold for *ln*

$\log 1 = 0$; $\ln 1 = 0$; $\ln 2 \approx 0.693$; $\ln 10 \approx 2.30$; $\ln a \approx 2.30 \log a$; $e^a \approx 10^{a/2.30}$; $\log e = 1/(\ln 10) \approx 0.43$; $e \approx 2.7$

$\log 2 \approx 0.30$; $\log 3 \approx 0.48$; $\log 4 \approx 0.60$; $\log 5 \approx 0.70$; $\log 6 \approx 0.78$; $\log 7 \approx 0.85$; $\log 8 \approx 0.90$; $\log 9 \approx 0.95$; $\log 10 = 1$.

The multiple choice questions with numerical answers included 8 - 10 answers per question, arranged in ascending or descending order so that the desired (or closest) answer can quickly be found. The idea behind having so many answers is to encourage the students to adopt the strategy of actually doing the calculation and finding their answers among those listed. Since some of the listed answers are the results of common errors, obtaining a value included among the answers does not mean that it is correct. Since so many answers are listed, one is not likely to correctly identify the one correct answer by relying entirely on the process of elimination or on rough estimates. It is hoped that this exam format encourages students to work hard at their homework and practice problems, to develop their facility at both the chemistry and the math.

For example, in the van't Hoff problem discussed above (#14 in the Appendix), noting that ΔH^o must be positive, since K_p increases with increased temperature, eliminates 4 of the answers listed. Noting that ΔH^o is likely to be large, since K_p increases so dramatically with increased temperature, eliminates another 2 answers. These are both useful insights and can help the student catch calculation errors. However, this still leaves 3 reasonable answers listed, so to identify the correct one, one must still do the calculation.

Often a question whose exact solution requires a calculator can be converted to a calculator-free multiple-choice question by spacing out the listed answers so that good estimates, to one or two significant figures, enable one to choose the correct answer as the closest one among those listed.

The potential advantages of encouraging students to train themselves to perform calculations on paper, rather than going right from the question to the calculator as is often done, are numerous. On paper, students may be more likely to include units with the numerical values in their equations, reminding them of the meanings of the numbers. They are more likely to use algebra to solve for an unknown, and to simplify products or ratios of expressions.

Most importantly, the most efficient way to check that one is avoiding numerical errors, in the absence of a calculator, is to think about the *meaning* of the numbers. For example, do we need the pH of a 2×10^{-4} solution of a strong acid? One can make a mental note that the pH must be *below* 4, not more than 4, since this is more concentrated than a 1×10^{-4} M solution, which would have a pH of 4. Constantly checking whether the calculations *make sense*, and making rough estimates, can reinforce the student's understanding of their meaning. This method of checking the calculations can provide much more conceptual insight than simply checking that one has plugged the correct numbers and functions into the calculator.

It is important for the instructor to model a sense of ease with the sort of pencil-and-paper (whiteboard and marker) techniques that we are urging the students to adopt. For most of us, who have become nearly as calculator-dependent as our students, this requires some practice.

To experience first-hand the pleasures of doing problems on equilibrium and acid-base reactions without a calculator, it is helpful for the instructor and teaching assistants to work some of the 38 problems included in the Appendix themselves. The topics of these problems are listed below.

Chemical Equilibrium

Problem	
# 1, 2	Ratios of changes from initial to equilibrium concentrations
# 3, 4	Given K and all but one equilibrium concentration, solve for the unknown one
# 5, 6	Calculate K for a given reaction, given K values for related reactions
# 7	Comparing Q (reaction quotient) to K to determine direction of spontaneity
# 8	Convert K to K_p (the equilibrium constant expressed in terms of partial pressures)
# 9	Calculate K given the initial concentrations and one equilibrium concentration
# 10, 11	Calculate the equilibrium concentrations, given K and the initial concentrations
# 12, 13	Calculate the equilibrium partial pressures, given K_p and the initial partial pressures
# 14	Use the van't Hoff equation to calculate ΔH^o, given K_p values at two temperatures
# 15	Given K_{sp} (solubility product constant), calculate the solubility of a slightly soluble salt

# 16	Given the solubility of a slightly soluble salt, calculate its K_{sp} value
# 17	Given K_{sp}, calculate the solubility of a slightly soluble salt in the presence of a solute with a common ion

Acid-Base Reactions, Buffers and Titrations

# 18, 19	Calculate the pH of a solution of a strong acid, given its concentration
# 20	Calculate the pH of a solution of a strong base, given its concentration
# 21, 22	Given the pH of a solution, calculate its OH^- concentration
# 23	Calculate the pH and pOH of water at a different temperature, given K_w
# 24, 25, 26	Calculate the pH of a solution of a weak acid, given its concentration and K_a
# 27	Calculate the K_a of a weak acid, given its concentration and the pH of the solution
# 28	Calculate the "percent dissociation" of a weak acid, given its concentration and the pH of the solution
# 29	Calculate the pH of a solution of a weak base, given its concentration and the K_a of its conjugate weak acid
# 30	Calculate the pK_b of a weak base, given its concentration and the pH of the solution
# 31	Buffers: calculate the pH of a solution with given numbers of moles of a weak acid and its conjugate weak base, given the K_a of the weak acid
# 32	Buffers: calculate the pH of a solution given the concentrations of a weak acid and (a lower concentration of) NaOH, and the pK_a of the weak acid
# 33, # 34	Buffers: calculate the pH of a solution with a given number of moles of a weak acid, its conjugate weak base, and strong base, given the pK_a of the weak acid.
# 35, # 36	Titrations involving strong acids and strong bases: calculate the pH of the solution after a given amount of the strong base (or strong acid) has been added
# 37, # 38	Titration of a weak acid by a strong base: calculate the pH of the solution after a given amount of strong base has been added

IID. Accommodating Students Who Suffer From Severe Math Anxiety or Discalculia

Some students are genuinely traumatized by the prospect of having to do calculations without a calculator under timed conditions (even if twice the usual time is allowed, as was the case for our calculator-free exams). One semester, a student obtained a letter from our Disability Resource Center, explaining that he had discalculia and that his accommodation required the use of a calculator.

For such students, it is better to excuse them from the calculator-free constraint, rather than to cause them excessive stress. It is useful to remember that not all of our students in general chemistry are planning careers in the STEM fields. Many students are required to take our introductory-level classes as part of majors which do not otherwise require these sorts of math skills. While desirable, forcing pencil-and-paper calculations on college students who find this prospect terrifying may only worsen their fear of math, and prevent them from developing an appreciation for chemistry. For such students, these interventions may have been much more effective much earlier in their educations.

III. Students' Evaluations of Calculator-Free Exams

In midterm and end-of-semester evaluations, students were invited to share their opinions of our calculator-free midterm exam "experiment". In general, as might be expected, the responses were mixed, with more negative than positive ones.

For example, for one class (Chem 1022, Spring 2011), some of the students' written comments on our calculator-free Exam 2 and associated math reviews and practice problems are listed below. Indeed, some of the students' complaints were justified. That semester, the average on our calculator-free exam was 56%, as compared with the 64% average for the other two midterms and the final exam. Although some correction was made for the lower class average on Exam 2 by curving the course grades upward at the end of the semester to give the usual class distribution, some individual students' grades were negatively affected by this calculator-free exam.

<u>Pro:</u>

"Calculator free test was an interesting idea. Like the math review. I'm glad we only had to do one of these exams - keep it this way."

"I think it was useful because it required more critical thinking and less "randomly plugging things into a calculator."

"I think it's good to do - too many people don't know basic math!!
Yes. Everyone should know basic computations w/o a calculator."

"Yes, I feel like it taught me to estimate magnitudes easier...Yes, I appreciated the fact that I had to learn logs and such."

"Honestly, I think the calculator-free exam is helpful because I've found that I along with others have become too calculator dependent. It also forced me to increase my comfort level with scientific notation, which had atrophied."

"I thought the calculator-free exam was a good idea. It helped me become less dependent on my calculator."

"It reminded me how dependent on my calculator I am...Yes, it was a good idea."

"I thought it was well worth it...By making the exam calculator-free, I studied very hard for this exam to make sure I would do well. I wish all were calc free to inspire the same panic!"

"I liked the calc-free test, I think it will help me on the math on the MCAT"
{Added note: The MCAT is the Medical College Admissions Test.}

"I don't think it will be particularly useful unless I take the GRE or MCAT, but I don't know about that yet. It's useful for the MCAT, from what I've heard."

"It was useful, strengthened math skills."

"Interesting idea. Very useful to teach how to do calculations in head."

"The calculator free aspect did not make it more difficult."

"Not having a calculator just made it take longer, not necessarily harder."

"I thought it was a fair test. It was somewhat useful but I don't think it will be that helpful in the future."

Con:

"It had reasonable meaning but it was difficult. I just finished Calc 1, 2, 3 & 4 but I kept blanking on basic math - I'm used to using TI-89 graphing calculator."

"Horrible. We have math classes for a reason! We would not be expected to do this math mentally in a lab when even high schools hardly teach pen + paper methods anymore."

"It was unfair that one of our exams was calculator-free. I didn't/don't agree that we had to do math/calculations by hand since this is not a math course (even math courses allow us to use calculators)."

"I was not a fan! My calculator was my security blanket!"

"The calculator free exam would've been more effective on an easier midterm, I found it hard to do acid-base stuff without one...It reminded me how dependent on my calculator I am."

"...But it is pointless. I spent more time remembering how to multiply neg exponents than studying chem & after the test I went back to the calc. (I did well on the exam in case you wonder.)

"The calculator-free midterm seemed pointless to me. It would have covered the same material if using a calculator but would have taken less time."

"I feel like we spent more time on math than chemistry. I do not think it was useful."

"I feel like I spent a lot of time trying to understand the math behind the questions, rather than the chemistry aspect. This test hurt my grade, but I guess I could have spent more time studying."

"This was my lowest test grade by far. I felt like I spent the majority of my study time trying to figure the math out and wasn't confident with the subject matter because I was focused on the math."

"I don't understand how useful calculator-free exams are, especially when logarithms are a major portion of it."

"I didn't like it because I was more worried about the math than the chem."

"Also the calculator-free exam I felt should have been free response so we are not punished for being not very good at math, but could receive partial credit for correct procedure."

"I did not agree with the calculator-free test "experiment." I felt it only decreased the value of the chemistry concepts because I focused more on memorizing log rules."

"I feel it would be of better use in higher level chemistry. Not a general chem."

"I didn't find this helpful. It was extremely stressful and distracted me from study the concepts + how to set up + perform the problems."

"It should not be done again. Just because I had an extra hour does not mean it helped."

"I don't think it will be useful in the future b/c I will always have a calculator and highly doubt I'll have to do logarithms in my head."

"I thought it was interesting to find out how dependent I am on my calculator.. I know I would have done better on this exam with a calculator. I think it isn't really useful. While it is important to know math, at this point, calculators are everywhere. Mental math isn't always the most efficient option. Estimating logs isn't useful."

"I thought not being able to use a calculator was very stressful and it made it more of a math test than a chem test...No, I will probably never be in a situation where I won't have access to a calculator."

IV. Broader Impacts

Many people share the sentiments of the last students quoted above: "I will always have a calculator," "calculators are everywhere," "I will probably never be in a situation where I won't have access to a calculator."

But, one might wonder whether a more mathematically fluent electorate might make different decisions about important political, social and environmental issues. Maybe we would even have elected a different president?

On the morning of election day, Nov. 8, 2016, it seemed likely that Hillary Clinton would win. According to the New Yorker, "On Tuesday morning, FiveThirtyEight's "polls-only" prediction model put the probability of Clinton winning the presidency at 71.4 per cent. And that figure was perhaps the most conservative one. The *Times*' Upshot model said Clinton had an eighty-five per cent chance of winning, the Huffington Post's figure was ninety-eight per cent, and the Princeton Election Consortium's estimate was ninety-nine per cent." [9]

Of the eligible voters who would have been strongly opposed to a Trump presidency, how many really understood these percentages and probabilities on an intuitive level? How many could make an informed decision of whether to vote for Hillary Clinton, or to skip voting and save a lot of time off from work or school on a Tuesday, or to "vote their conscience," since Hillary Clinton was so likely to win that she didn't need their vote?

On a less consequential note, one may have noticed an odd feature in the media reporting about a year earlier, concerning a drug, Daraprim, whose cost had skyrocketed.[10] It seemed that every time this story aired on TV, the reporter said that the price had increased by "5,500 percent". One might wonder why they did not sometimes say that it had increased 55 times, or by a factor of 55, which both seem to be simpler ways of saying the same thing, and would allow them to vary the wording. Did they want their audience to think that it had increased by a factor of 5,500? (Isn't a factor of 55 bad enough?) Or, did the reporters and writers themselves not understand that 5,500% is the same as 55 times?

To help answer this question, the following question was added to our Spring 2016 calculator-free Math Assessment:

==========

In September 2015, we read as headline news, "drug price increases 5,000 percent overnight".

If a pill initially costs $1 and then the price increases 5,000%, what is the new price?

- A. $500,000
- B. $50,000
- C. $5,000
- D. $500
- E. $50
- F. $5

Answer: **E.** **$50**

==========

Surprisingly, the correct answer, $50, was chosen by only 56% of the students, and 32% chose $5,000. So, about one-third of the students in this second-semester chemistry class at a fairly selective state university thought that 5,000% means an increase of 5,000 times.

Now back to Election Day. If the news media reported that Hillary Clinton had an 85% chance of winning, how many readers and listeners thought that this meant that she was **85 times** more likely to win than was Donald Trump? How many commentators, writers and politicians shared this math misconception, and how might it have influenced their reporting and related activities?

If one-third of our college chemistry students interpret "percent" to mean "times", isn't it likely that this math misconception is *at least* as prevalent in the general electorate? Yes, we always have access to a calculator. But, how many people pulled out their calculators to calculate that 85% / 15% is only a factor of 5.6? If more people had understood that the chances were better than 1 in 6 that Donald Trump would actually become president, might more of the non-voters and third party voters have realized, as Al Gore emphasized, that their votes really counted?

As it turned out, Clinton lost the election due to a total of about 80,000 votes (0.08 million) in three swing states,[11] while winning the national popular vote by more than 2.8 million out of 137 million votes cast for president.[12] More than 90 million people who were eligible to vote chose not to,[13] and 8 million voted for other people, who had no chance of winning the election.[12]

Recently, Hillary Clinton has been reported to say, “Not so much anymore, but in the immediate aftermath, from after the election to probably the first of the year, ... I had people literally seeking absolution... ‘I’m so sorry I didn’t vote. I didn’t think you needed me.’ I don’t know how we’ll ever calculate how many people thought it was in the bag, because the percentages kept being thrown at people — ‘Oh, she has an 88 percent chance to win!’ I never bought any of that, but lots of people did.” [14]

The price we pay for a mathematically illiterate electorate can be steep. People often make critical decisions involving numbers based mainly on gut feelings and intuitions, without first consulting their calculators. As high school and college chemistry teachers, we can do our parts to encourage our students to develop a deeper level of mathematical fluency. This skill can better inform not only their future academic and career activities, but also the feelings and intuitions that will influence some of their most consequential decisions.

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