UNIT 6: THE MATH OF CHEMISTRY

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How was Avogadro's number determined?

Feb 16, 2004 | **Chemist George M. Bodner of Purdue University explains.**

Contrary to the beliefs of generations of chemistry students, Avogadro¿s number--the number of particles in a unit known as a mole--was not discovered by Amadeo Avogadro (1776-1856). Avogadro was a lawyer who became interested in mathematics and physics, and in 1820 he became the first professor of physics in Italy. Avogadro is most famous for his hypothesis that equal volumes of different gases at the same temperature and pressure contain the same number of particles.

The first person to estimate the actual number of particles in a given amount of a substance was Josef Loschmidt, an Austrian high school teacher who later became a professor at the University of Vienna. In 1865 Loschmidt used kinetic molecular theory to estimate the number of particles in one cubic centimeter of gas at standard conditions. This quantity is now known as the Loschmidt constant, and the accepted value of this constant is 2.6867773×10^{25} m^{-3}.

The term "Avogadro¿s number" was first used by French physicist Jean Baptiste Perrin. In 1909 Perrin reported an estimate of Avogadro¿s number based on his work on Brownian motion--the random movement of microscopic particles suspended in a liquid or gas. In the years since then, a variety of techniques have been used to estimate the magnitude of this fundamental constant.

Accurate determinations of Avogadro¿s number require the measurement of a single quantity on both the atomic and macroscopic scales using the same unit of measurement. This became possible for the first time when American physicist Robert Millikan measured the charge on an electron. The charge on a mole of electrons had been known for some time and is the constant called the Faraday. The best estimate of the value of a Faraday, according to the National Institute of Standards and Technology (NIST), is 96,485.3383 coulombs per mole of electrons. The best estimate of the charge on an electron based on modern experiments is $1.60217653 \times 10^{-19}$ coulombs per electron. If you divide the charge on a mole of electrons by the charge on a single electron you obtain a value of Avogadro¿s number of $6.02214154 \times 10^{23}$ particles per mole.

Another approach to determining Avogadro¿s number starts with careful measurements of the density of an ultrapure sample of a material on the macroscopic scale. The density of this material on the atomic scale is then measured by using x-ray diffraction techniques to determine the number of atoms per unit cell in the crystal and the distance between the equivalent points that define the unit cell (see *Physical Review Letters*, 1974, 33, 464).

ChemHistory

Cleopatra's Perfume Factory and Day Spa

Nestled at the south end of the Dead Sea, Cleopatra's Day Spa is more than just a relaxing destination. It is an intoxicating experience designed to provide an escape from the pressures of everyday life. We hold an unmatched reputation and an elite clientele—Mark Antony marched his army to the Dead Sea to secure the spa for beautiful Queen Cleopatra. If our services work for a Queen and Roman Consul, just imagine what they'll do for your health and wellness. Specially trained therapists assess your current level of fitness and discuss your goals. Our most popular packages:

Package 1: "The Cleopatra"

45 silver denarii

*Package includes full use of the spa's facilities and your choice of three of the following:

DEAD SEA MUD BODY POLISH deep cleans, purifies, and restores your skin, leaving you feeling smooth and radiant all over.

CROC EXCRETA FACIAL tightens the pores and stimulates circulation so your skin is left with a smooth, healthy glow.

DEAD SEA SALT SCRUB exfoliates and revitalizes the skin by drawing out toxins.

MORINGA MANICURE leaves your hands feeling fresh and revitalized, not greasy.

ASS-MILK BATH nourishes the skin and leaves it feeling soft and lithe.

OUR SIGNATURE MAKEOVER includes expertly applied green malachite and black galena eyeliner, red ocher and henna body paint, finishing with our exclusive crushed beetle-shell glitter for that Cleopatra look your own Mark Antony will love.

Package 2: "The Mark Antony"

30 silver denarii

*Package includes full use of the Cleopatra Day Spa facilities and your choice of two of the following:

DEAD SEA MUD BATH relieves aches and pains, reduces stiffness and muscle tension after exercise, and revitalizes the skin. Enriched with Dead Sea salts, our mud has a young, masculine fragrance.

ASPHALITE HAIR PACK alleviates dandruff and normalizes oily hair. Makes hair feel revitalized and moisturized. It will not overdry the scalp.

DEAD SEA SALT FOOT SCRUB is just the thing after marching with your legions.

HORSERADISH BODY POLISH revitalizes your skin without that smelly, greasy afterfeel.

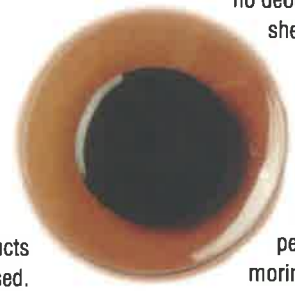
BLACK-TAR MASK draws out toxins to clear up unsightly facial blemishes, purifies, and revitalizes the complexion.

Cleopatra, famous Queen of Egypt, ascended to the throne at the age of 17. She later owned a perfume factory and recorded recipes for early cosmetics—many used early chemical techniques.

By Lois Fruen

These real treatments from our fictional ancient spa brochure, (on the previous page), may not seem appealing, but they were sought after in ancient times, and many are still available today, albeit with different names. It was Cleopatra, the famous queen of Egypt, who popularized skin care treatments in her book titled *Cleopatra Gynaeciarum Libri.* There, she recorded recipes for making cosmetics and perfumed ointments. She was so interested in spa treatments and perfumes that her lover, Mark Antony, gave her the gift of a spa and perfume factory that had been built by Herod the Great at the south end of the Dead Sea.

Asphalt skin care



Archaeologists unearthed jars at Cleopatra's spa that contained residues of ancient skincare products that Cleopatra likely used. When chemists analyzed the residue from one jar of Dead Sea mud treatment, they were surprised to find it had a similar chemical composition to asphalt, better known as tar or pitch, a complex mixture of high molecular weight hydrocarbons, with partially oxidized and sulfur-containing compounds mixed in for good measure. Their analysis was confirmed by Pliny the Elder, a first-century AD historian, whose histories tell us that ancient spa treatments started with an application of asphalite mud followed by a treatment of Dead Sea salt.

COREL

Imagine Cleopatra submitting to being smeared in muddy tar and then having the tar rubbed off her skin with bath salts. Pliny also tells us that perfume was used to cover the smells of the pitch and salts. Boy, would Cleopatra have needed perfume after a spa treatment like that!

Perfumes

For Cleopatra, perfumes were important not just for masking the smells of skin treatments but to cover offensive body odors. Cleopatra would have carried small containers of her perfumed ointments and powdered perfumes that she would have reapplied several times a day to keep her complexion looking fresh and her skin sweet smelling. Remember that there were no deodorants available in her time, and she lived in a hot climate.

Chemists have reconstructed a number of ancient perfumes using Cleopatra's own recipes and analysis of perfume residues found in jars from Cleopatra's spa. They discovered that Cleopatra favored perfumed ointments made from moringa oil or horseradish oil (*Moringa pterygosperma* or *M. aptera*). Those ointments would have disappeared into her skin quickly and left no greasy feeling behind. Moringa oil is still used in Persian perfumes today, and chemists at L'Oreal have recreated ancient Egyptian perfumes using moringa oil.

PHOTODISC

Before you sneer at the spa treatment using asphalite, Dead Sea mud skin care products and bath salts are still marketed today. In fact, some of the finest spas advertise wraps and facial masks made from mud and Dead Sea salt.

Two Minneapolis students from the Breck School, Stacy White and Caroline Kaylor, made a project of trying to recreate ancient perfumes. They used natural materials such as lard (as a nonpolar solvent) to extract fragrant organic molecules from rosemary and borneal heather.

Other chemists have followed Cleopatra's ancient recipes that call for mixing herbs, flower petals, leaves, or seeds with hot vegetable oil made from pressed olives. They let the mixture soak for a week at 30–40°C. Then, they pressed the mixture through a cloth bag to extract the perfumed oil from the pressed olive mixture. Besides using perfumes made with olive oil to anoint herself, Cleopatra may also have added perfumed oils to her wine to give it a more pleasant smell since those made with olive or vegetable oils were edible.

PHOTODISC

You may have heard the saying, "Flies in the ointment." It comes from a very real problem in Cleopatra's spa. Flies were ever-present in Egypt and the near east, and they were attracted to the fats and oils used to make perfumes. The flies would get trapped in the perfumed oint-

ment and die. The ointment putrefied as the flies decomposed, giving off a foul odor that spoiled the batch. Even the Bible makes reference to this in Ecclesiastes 10:1. "Dead flies make the perfumer's ointment give off an evil odor ...". The odor is the result of the chemical breakdown of the proteins that produce diamines called **putrescine** and **cadaverine**. The names of these two amines are appropriate—they smell like rotting bodies. They can also contribute to bad breath and the less-than-desirable body odors that made the use of perfumes so necessary in ancient times.

$NH_2CH_2CH_2CH_2CH_2NH_2$

putrescine

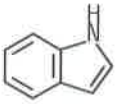
$NH_2CH_2CH_2CH_2CH_2CH_2NH_2$

cadaverine

COURTESY OF BRECK SCHOOL

The results of their project? Good ... *if* you like fragrant lard! Stacy and Caroline suggest that further work exploring the effects of temperature, light, and other solvents such as olive oil is necessary.

Besides perfumed essential oils, Cleopatra used powdered excrement from Egyptian crocodiles to clean and embellish her complexion. This is not as odd as it sounds.



indole

Indole, used to moderate modern-day perfumes, is derived from feces, and urea, a component of urine, is used in modern skin-care products.

To keep her skin soft and supple, Cleopatra bathed in milk of asses, having discovered an important property of protein in a fatty emulsion—it contains lactic acid that is an alpha-hydroxy acid which breaks down dead skin cells. Today, you can buy foaming milk baths, and a number of modern skin-care products contain lactic acid.

Cleopatra painted her eyes with green and black pigments to protect her eyes from those ever-present flies and to enhance her appearance. On special occasions, she may have added glitter made from crushed beetle shells mixed with her eye paint. And she would have cleaned her teeth with natron, a natural form of baking soda, and freshened her breath with spearmint.

GETTY IMAGES

When chemists used crystallographic and other chemical tests to analyze the residues of ancient eye makeup, they found that the green eye makeup contained malachite, which is hydrated copper(II) carbonate ($CuCO_3{\cdot}5H_2O$). They discovered that the black eye paint, called kohl, contained galena, a gray-lead ore of lead(II) sulfide (PbS), and cerussite, which is lead(II) carbonate ($PbCO_3$). The kohl also contained laurionite (PbOHCl) and phosgenite ($Pb_2Cl_2CO_3$). These last two chemicals were unexpected, because they do not occur naturally; ancient Egyptians had to synthesize them. Following recipes reported by Pliny, chemists duplicated ancient methods for making kohl by crushing PbO with natron (Na_2CO_3) or rock salt (NaCl) and then filtering the mixture and repeating the process over the course of several weeks. The rock salt produced PbOHCl, while the carbonate resulted in $Pb_2Cl_2CO_3$. Modern-day chemists say these syntheses developed by ancient Egyptians were the first "wet-bench" chemistry ever done.

PHOTODISC

Cleopatra would have dyed her nails, hands, and feet and perhaps her hair with henna from a shrub called Egyptian privet (*Lawsonia alba*). Henna is a reddish-brown organic dye that was used in Turkey as early as 7000 B.C. In Cleopatra's time, henna could have been applied as a paste or by a more complex formulation using oil, sugar, and citric acid. Henna is still used today for temporary tattoos and by a variety of cultures to signify a woman's fertility.

COURTESY OF BELOIT COLLEGE, LOGAN MUSEUM

Finally, Cleopatra would have stored her perfumed oils and cosmetics in attractive jars that were designed to hold skin care products and pigments. Archaeologists have discovered hieroglyphs on similar jars that advertise the benefits of using the product. Some things just don't change!

Lois Fruen teaches chemistry at the Breck School in Minneapolis, MN. Her article "Copper Verdigris: A Women's Art" appeared in the February 2003 issue of *ChemMatters*.