Determination of the Avogadro Constant

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Measurements are reported on the densities and isotopic-abundance ratios of nearly perfect Si single crystals. These, when combined with optical interferometry of the crystal repeat distance, yield a new value for the Avogadro constant. This result, $N_A = 6.022\,0943 \times 10^{23}$ mol^{-1} (1.05 ppm), represents a more than thirty-fold reduction in the uncertainty of previous direct measurements.

We have measured the densities, isotopic abundances, and lattice parameters for some highly perfect Si crystals. Our measurements improve on those previously made in that they are independent of an assumed density for water; they do not employ an x-ray wavelength scale; and they involve "absolute" isotopic-abundance determinations, i.e., abundances were measured against synthetic ratio standards. They yield a new value for the Avogadro constant, as follows from the equation of Bragg,[1] viz., $N_A = nA/\rho a_0^3$, where n atoms of average atomic weight A occupy a unit-cell volume a_0^3 and ρ is the macroscopic density. Here, we report these new results, reconcile them with overtly discordant ones obtained by previous workers, and consider some implications regarding present knowledge of the fundamental constants.[2]

Limitations of density determinations which use water as a standard are suggested by the 6-ppm difference in the only two available "first-principles" measurements.[3] We have, instead, made use of readily available, highly spherical steel artifacts as local and temporary "standards" of density. Their masses were determined in terms of the U. S. national standard (kilogram replica number 20) by well understood procedures.[4] Volumes at temperatures referred to the International Practical Temperature Scale-1968 were inferred from diameters measured by interferometry using a hollow Fabry-Perot etalon[5] illuminated by a He-Ne (633 nm) laser calibrated in terms of a ^{86}Kr lamp approximately realizing the present definition of length.[6]

We compared the densities of these spheres with those of four 200-g Si objects (X_2, X_3, X_4, X_5) in a highly redundant (24 intercomparisons) hydrostatic determination in a fluorocarbon immersion medium.[7] Subsequently, three rather perfect specimens, D_1, D_2, D_3, were compared with X_2, X_3, X_4, X_5 in twelve hydrostatic measurement cycles. Each trial using two of the "X" crystals and two of the "D" crystals gave relative volumes for the pairwise combinations. Least-squares values for the densities are given in Table I in the second column.

Observed densities need to be corrected for the presence of C and O in D_1 and D_2. As found by current procedures[8] of the American Society for Testing and Materials, D_3 was clean while the D_1 and D_2 material had oxygen at 6.0×10^{16}/cm^3 and carbon at 3.9×10^{16}/cm^3. The fractional density change due to introduction of an impurity can be written $\Delta\rho/\rho = \Delta A/A - 3\Delta a/a$. For oxygen, there is an expansion, $\Delta a/a$, of $3.8\times10^{-24} n_O$[9] and for carbon a contraction of $6.5\times10^{-24} n_C$,[10] where n_O and n_C are the respective number densities (cm^{-3}). For interstitial O, the net density change is nearly zero while for substitutional C, there is a net increase of 0.31 ppm. This correction was applied to obtain the "corrected" densities for D_1 and D_2 listed in Table I.

Isotopic-abundance measurements for the specimens D_1, D_2, and D_3 were carried out relative to another large homogeneous specimen which was wafered to form a publicly available Standard Reference Material, SRM 990.[11] This comparison was effected by the use of a 15-cm 60° magnetic sector mass spectrometer using the abundance procedure described by Smith, Shields, and Tabor[12] and by Rodden.[13] To obtain absolute values of the abundance ratios the mass spectrometer was calibrated by using known mixtures prepared from chemically pure and nearly isotopically pure separated isotopes. From the absolute isotopic ratios, the atomic weight of the

TABLE I. Densities of Si crystals and estimated components of error. The estimate for σ_T contains contributions from σ_m and the following other sources in ppm: temperature of interferometry (0.23); wavelength calibration (0.08); phase shift on reflection (0.12); photographic nonlinearity (0.01); bath temperature (0.03); mass of steel balls (0.18); mass of Si crystals (0.05); balance calibration (hydrostatic) (0.27). The larger error in the case of D_3 is due to small sample size.

Sample	Obs. density (g/cm^3)	Corr. density (g/cm^3)	σ_m (ppm)	σ_T (ppm)
D_1	2.3289917	2.3289910	0.22	0.48
D_2	2.3289906	2.3289899	0.44	0.62
D_3	2.329 0003	2.329 0003	0.94	1.04

reference and thus of samples D_1, D_2, and D_3 can be calculated using the nuclidic masses reported by Wapstra and Gove.[14] The complete details of these measurements will be reported elsewhere.[15]

Results of the measurements of the absolute isotopic abundances of SRM 990 are given in Table II along with provisional error estimates. The principal limitations in the precision and accuracy obtained here arise from the difficulty in measurement of the very small amount of the minor isotopes present in the separated isotope preparations because of the very small amount of ^{30}Si available (ca. 100 mg). Table II also gives the results for the crystals D_1, D_2, and D_3. These were obtained from measurements of the differences $A(990)-A(D_3)=0.68$ ppm, $A(D_1)-A(D_2)=0.75$ ppm, and $A(D_3)-A(D_2)=4.54$ ppm. These comparisons do not contribute significant additional uncertainty.

Data in Tables I and II may be combined to give estimates of the formally invariant quantity A/ρ. These are listed in Table III with standard deviations derived from repeated observations and estimates of uncontrolled systematic variability. The results are sufficiently concordant that a weighted average seems appropriate. It appears to be of considerable significance that, while both density and atomic weight values spread over 5 ppm, the A/ρ ratios lie within 0.3 ppm.

The lattice parameter (and hence the volume of a unit cell) was obtained by means of simultaneous x-ray and optical interferometry of a common baseline for a sample of the crystal D_3 only.[16] Measurement accuracy has recently been improved by use of an iodine-stabilized laser[17] and direct measurement of the cavity length to permit evaluation of the Fresnel phase shift.

The Fresnel-phase-shift correction accounts

TABLE II. Abundances and atomic weights for SRM 990 and the samples D_1, D_2, and D_3. Abundances for SRM 990 were obtained from measurement of the ratios ^{28}Si/^{30}Si and ^{29}Si/^{30}Si. Abundances for the D crystals were obtained by difference measurements as indicated in the text. The error contributions in ppm: mixing separated isotopes (0.30); separated isotope ratio (0.30); SRM 990 ratio (0.59)—yielding $\sigma_T=0.73$ ppm.

		SRM 990 Isotope	
	^{28}Si	^{29}Si	^{30}Si
Atomic %	92.228948	4.669981	3.101071
Nuclidic mass	27.9769286	28.9764969	29.9737722
Weight %	91.872310	4.818128	3.309562
	A(SRM 990) = 28.085 532(21)		
	D_1	D_2	D_3
Atomic weights	28.085406	28.085385	28.085513

TABLE III. Values for the formally invariant quantity A/ρ for each of the "D" crystals at 25°C.

Sample	A/ρ	σ_m (ppm)	σ_T (ppm)
D_1	12.059 0444	0.48	0.88
D_2	12.059 0411	0.62	0.96
D_3	12.059 0422	1.03	1.27
Weighted mean	12.059 0427	0.53	0.75

for the fact that the distance traveled in a scan from cavity length L_1 to L_2 differs from the change in optical order number by[18] $\cos^{-1}[(1-L_2/R)^{1/2}]-\cos^{-1}[(1-L_1/R)^{1/2}]$ for the hemispherical geometry used here, with curved mirror radius R. We determined L by measuring the distance δL (using x-ray interferometry) between microwave sidebands of the visible radiation differing in frequency by a known interval 2ω near 20 GHz,[19] i.e., $L=c\delta L/2\omega\lambda$. The order numbers obtained (ca. 1000) were essentially exact. An uncertainty of 1 order number would contribute less than 0.01 ppm to the lattice-constant uncertainty.

Each lattice-parameter–determining run was corrected for Fresnel phase shift and for departure of the measurement temperature (determined by well calibrated small thermistors in close proximity to the crystal) from the reference temperature (25°C) by using $\alpha=2.56\times10^{-6}$ K^{-1}.[20] From 165 determinations, a standard deviation of the mean, σ_m, is obtained as 0.03 ppm. Error estimates for this lattice-parameter measurement are given in Table IV. The indicated value $a_0=0.543\,106\,61$ nm (0.25 ppm) corrected to 25°C gives a unit-cell volume, $a_0^3=0.160\,197\,33$ nm^3 (0.75 ppm).

The final result is thus at hand: We combine the determination of A/ρ and that of a_0^3 to obtain $N_\mathrm{A}=6.022\,094\,3\times10^{23}$ mol^{-1} (1.05 ppm). The uncertainty is taken as the square root of the sum of the squares of that associated with A/ρ and that associated with a_0^3 and is intended to reflect our estimate of 1 standard deviation for a hypothetical replication of our total procedure.

TABLE IV. Lattice-parameter–determination results and error contributions. The estimated error contributions in ppm: relative optical-x-ray interferometer drift (0.20); laser (product of order number and estimated first-derivative lock instability) (0.13); temperature (0.02); Fresnel phase shift (0.01); σ_m (standard deviation of mean) (0.03).

Laser wavelength (pm)	632 990.0742 ±0.0009
Fringe count ratio	1648.2641 (0.25 ppm)
a_0 (25°C)	543.106 61 (0.25 ppm)

There is no previous result to which the present one may be properly compared since all of these were referred to an x-ray scale, i.e., the measured quantity was $N_\mathrm{A}\Lambda^3$ where Λ is the conversion factor from x-ray scale to angstroms. A comparison is nonetheless possible with one outstanding representative of this class of measurement[21] by translating the present result to an x-ray wavelength scale. Also, we can compare our result with an indirect value for N_A obtained from electrical measurements.[2]

In the case of the x-ray measurements (basically a_0/λ determinations) reported in Ref. 21 there is substantial agreement. Densities given in Ref. 21 are referred to that of water which is assigned the value obtained by Tilton and Taylor.[3] These results group about 6 ppm above those reported here. Our peripheral work on water has indicated that the values obtained by Thiessen, Schell, and Disselhorst[3] lie closer to observed values on local water. Hence, the densities reported in Ref. 21 might be reduced by a few parts per million which would lead to better agreement with our results. There is not much impact on N_A here since the results of Ref. 21 require use of Λ and involve unknown isotopic abundances for Si.

The indirect value of $N_\mathrm{A}=6.022\,045\times10^{23}$ mol^{-1} from the least-squares adjustment[2] has a 1σ uncertainty of 5.1 ppm. The discrepancy between the indirect value and that reported here is 8.2 ppm or 1.6σ. A more relevant statement is that introducing this new result into the least-squares adjustment of all the constants[2] changes the Birge ratio from 0.83 to 0.89,[22] suggesting that at present further analysis is not needed.

It is possible to make certain speculations about what further improvements are possible in this type of measurement. Use of enriched ^{28}Si, say 99%, and present mass spectroscopic procedures would give the atomic weight to 0.01 ppm. New processing techniques appear capable of reducing the vacancy cluster problem.[23] Transfer from artifact mass and volume to crystal density could be made at the 30-kg level yielding 0.01-ppm densities for an aggregation of material which need not be isotopically enriched or highly perfect. Subsequent ordering of these specimens via a Cartesian diver apparatus[24] or with density columns using certain newly available liquids would permit 0.01-ppm transfers to ca. 100-g specimens of enriched material. Controllable systematic effects in the x-ray/optical interferometer could be reduced to a level below 0.01 ppm (the precision is already at hand). It would thus appear that a value of N_A is obtainable with an uncertainty of the order of 0.01 ppm. Should this be achieved, one might wish to assert that the artifact kilogram is redundant and that masses can be obtained via an algorithm of realization from the atomic mass unit.

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