Letters to the Editor

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Variety of Our Sources of Information on Avogadro's Number and Other Constants*

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IN a recent article[1] Straumanis has stated that the most precise value of Avogadro's number, N, is obtained by means of crystal lattice parameter and crystal density measurements. In support of this statement he cites articles[2] by Birge in 1942 and by Stille, 1943 and 1948. One of the chief purposes of this note is to emphasize the fact that this statement is definitely no longer true, a circumstance which, undoubtedly, most physicists and physical chemists do not yet realize. We here enumerate no less than thirteen different ways of obtaining N beside the one cited by Straumanis, all of comparable accuracy. The method cited by Straumanis employing grating values of x-ray wavelengths to measure crystal parameters we shall refer to as the x-ray-crystal-density method or, for brevity, the X.R.C.D. method. Of the thirteen other methods ten are more accurate than the X.R.C.D. method, and the most accurate of the fourteen has nothing whatever to do with crystals but involves such diverse experimental information as the Faraday by electrochemistry, the "omegatron" (or inverse cyclotron) determinations of the magnetic moment of the proton, the Rydberg constant, and the fine structure splitting in deuterium. For this reason we believe that Straumanis' proposal to conventionalize the value of N on the basis of the density and lattice parameter of "purest calcite" would be an extremely arbitrary and objectionable step.

For the sake of brevity we here adopt the same symbols and equation numbers used in a recent paper[3] by the authors. The thirteen independent equations on page 701 of that paper, Eqs. (8.1) to (8.13), comprise a statement of the bulk of our present precise information bearing on the constants and conversion factors of physics, their sources being indicated by the numbers in parentheses and in brackets to the left of each equation. We shall work, however, with the linearized forms of these Eqs. (8.14) to (8.26) on page 702 of reference 3. We adopt a fixed value for the velocity of light ($x_2=10$ or $c=2.99793\times10^{10}$ cm sec^{-1}), thus eliminating one of the five variables and two of the thirteen equations. We further simplify by combining all equations of the same kind such as the pair (8.16) and (8.17) or the triplet (8.22), (8.23), and (8.24), equating each kind to a weighted average value of the numerics. This gives the following seven equations in the four unknowns, x_1, x_3, x_4, x_5, corresponding to α, e, N and λ_g/λ_s. The numbers on the left refer to the observational data in reference 3 on which each equation reposes.

(6.2)(6.3)(6.4)	$x_3+x_4 = 84.2\pm10.9=a_1.$
(6.2)(6.5)(6.6)[7.5][7.6][7.8][7.9]	$-3x_1+2x_3+x_4 = 145.0\pm10.5=a_2.$
(6.2)(6.7)[7.5][7.6][7.8][7.9]	$3x_1-x_3 = -23.\pm22.9=a_3.$
(6.8)	$x_5 = 0.0\pm30.1=a_4.$
(6.2)(6.9)(6.10)(6.11)[7.7]	$-x_1+x_3-x_5=-65.4\pm29.5=a_5.$
(6.12)	$x_4+3x_5= 35.\pm37.8=a_6.$
(6.2)(6.13)[7.3][7.4][7.5]	$2x_1 = 80.\pm9.0=a_7.$

Even after this simplification the numbers of solutions for α, e, N, and λ_g/λ_s which can be formed from appropriately chosen subsets of these seven equations are no less than 11, 11, 14, and 11, respectively. We list below[4] only the solutions for x_4 (i.e., for N) in the order of increasing accuracy:

	(s.d.)
$x_4=(6a_2-12a_5-4a_6+3a_7)/2$;	$N=0.602980\pm0.000118.$
$x_4=3a_3+3a_5+a_6-3a_7$;	$N=0.602217\pm0.000073.$
$x_4=2a_1-a_3-3a_5-a_6$;	$N=0.602712\pm0.000061.$
$x_4=a_6-3a_4$; (X.R.C.D. solution)	$N=0.602521\pm0.000059.$
$x_4=a_1+a_2-3a_5-a_6$;	$N=0.602735\pm0.000058.$
$x_4=(2a_2-4a_4-4a_5+a_7)/2$;	$N=0.602619\pm0.000051.$
$x_4=(a_1+a_2-3a_4-3a_5)/2$;	$N=0.602628\pm0.000044.$
$x_4=(2a_1-a_3-3a_4-3a_5)/2$;	$N=0.602617\pm0.000039.$
$x_4=(2a_2+a_3-3a_4-3a_5)/2$;	$N=0.602639\pm0.000039.$
$x_4=(6a_1-6a_5-2a_6-3a_7)/4$;	$N=0.602588\pm0.000031.$
$x_4=(2a_2+4a_3-3a_7)/2$;	$N=0.602487\pm0.000030.$
$x_4=(2a_1-2a_4-2a_5-a_7)/2$;	$N=0.602566\pm0.000026.$
$x_4=(2a_1+2a_3-3a_7)/2$;	$N=0.602465\pm0.000017.$
$x_4=(4a_1-2a_2-3a_7)/2$;	$N=0.602442\pm0.000017.$

These results are also shown in Fig. 1.

The subscripts to the a's indicate the subset used in each solution. Most emphatically we do not recommend any of the above just-determinate solutions because each utilizes only a fragment of our total budget of information and arbitrarily ignores the remainder. It would also be a serious error in principle to take an ordinary weighted average of these solutions, using weights inversely as the square of the error measures, because the solutions are not independent but are observationally correlated. The fourteen solutions cannot, of course, be independent since there are only seven independent input data. Nevertheless, any one of these solutions has just as good a claim to validity as the X.R.C.D. solution.

Undoubtedly at least some of the observational data still contain small systematic errors and we are working on the difficult problem of detecting, if possible, where these are by exploration of the consistency measures, χ^2, of all possible overdetermined subsets by digital computer. The normalized residues, R_i/σ_i listed in Table III, page 702, reference 3, are so small, however, that we feel there is at present no sufficient criterion for rejection of any of the input data used in our November 1952 least-squares adjustment.[3] We recommend our least-squares adjusted values ($N=0.602472\pm0.000036)\times10^{24}$ (g mole)$^{-1}$) in preference to any just-determinate single track solutions (such as X.R.C.D.) because the least-squares adjustment makes the least arbitrary and most impartially inclusive use of all our sources of knowledge at any given epoch. It is most gratifying to observe the good compatibility of results derived from such diverse sources of information, for it gives a direct proof of the inner consistency of physical units beyond the arbitrariness of man-made cgs units.

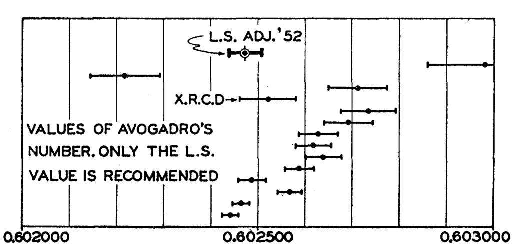

FIG. 1. The least-squares adjusted 1952 value of Avogadro's number (top) compared with fourteen just-determinate values each of which is based on a different subgroup combination of seven distinct and independent types of experimental measurement. Only the least-squares adjusted value is recommended.

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[1] M. E. Straumanis, Phys. Rev. **92**, 1155 (1953).
[2] R. T. Birge, Phys. Rev. **62**, 301 (1942); U. Stille, Z. Physik **121**, 142 (1943); **125**, 174 (1948).
[3] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **25**, 691 (1953).
[4] These values of N are per g-mole on the physical scale of atomic weights and should be followed by 10^{24}.