PHYSICAL REVIEW VOLUME 92, NUMBER 5 DECEMBER 1, 1953

Absolute Value of Avogadro's Number and the Soundness of Crystals

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(Received March 30, 1953; revised manuscript received September 8, 1953)

The experimental determination of Avogadro's number by the x-ray-density method is uncertain because of imperfections in crystals. It is proposed to regard the lattice of purest calcite as a reference lattice because of its proximity to a sound lattice, and to accept the value $N_0=6.02567\times10^{23}$ g mole^{-1} (phys.) which is equivalent to 6.02403×10^{23} g mole^{-1} (chem.) for Avogadro's number as derived from measurements on pure calcite. The perfection of the lattices of all other crystalline substances then would be determined in comparison with the calcite as either sound (equal in perfection to that of calcite) within the error limits or as defective (vacancies, interstitial atoms), using the number above for the calculations.

The most precise value for Avogadro's number is obtained, as already pointed out by other authors,[1] by means of lattice parameter and density measurements in applying the equation

$$N=nM/dv, \qquad (1)$$

n being the number of atoms or molecules per unit cell; M the atomic or molecular weight of the substance under investigation; d the density (in g/cm^3); and v the volume of the unit cell (in cm^3). While d and v can be determined to a high degree of accuracy by steadily improving experimental methods, the value of n is somewhat uncertain. Because of imperfections in crystals,[2] n, as the average of a great number of unit cells, might not be an integer but instead a quantity very close to an integer. If the real n is slightly larger than the closest integer (interstitial atoms in the crystal) which is substituted for n, a smaller value for N will be obtained. The reverse relationship holds in the case where there are vacancies in the crystal. N determinations by Eq. (1), using a larger number of different substances, may also not solve the problem, for vacancies are more frequent than interstitial atoms in crystal lattices.

Therefore, in order to obtain the correct Avogadro's number, it is necessary to know the number of imperfections per g atom or per g mole of the crystalline substance. Such a determination, of course, should not be made by the x-ray method, but by an independent method, for instance by conductivity measurements.[3] Unfortunately, such estimations are very uncertain. Consequently, it seems there is no way for the precise determination of the absolute number N_0 to be made, unless a method is found, other than the x-ray, for the exact determination of the extent of lattice defects in crystals.

However, there is still a possibility of solving the problem by agreement. If it is found that a certain substance has a lattice which in its perfection may be very near to a sound lattice (a sound lattice being defined as one with no vacancies and no interstitial atoms), the absolute Avogadro's number N_0 can be calculated by careful density and lattice parameter measurements. Since we now have the absolute Avogadro's number, the x-ray molecular weight M_x of other crystalline substances can be determined, using the same Eq. (1). If one compares these weights with the chemical weights M, one can estimate the number of defects D per g mole of the respective substance[4]

$$D=N_0(M_x-M)/M \text{ (chem. scale)}.$$

With D positive there are interstitial atoms in the lattice; with D negative vacant sites are predominant. If, within the error limits, $M_x-M=0$, then the lattice of the substance is as perfect as that of the reference or normal substance used for the determination of N_0: the lattice is sound. In case there happen to be submicroscopic regions with vacancies and interstitial atoms in equal amounts within the same crystal, then the crystal would appear sound if we apply the above method. However, such a distribution of imperfections is unlikely, especially after heat treatment of the crystals.

The imperfection I of a crystalline substance, that is the ratio of the numbers of imperfect sites to all sites, can also be determined simply by

$$I=(M_x-M)/M, \quad \text{or} \quad (N_0-N)/N, \quad \text{or} \quad (d-d_x)/d_x,$$

if one prefers to calculate from x-ray data the value of N for the substance, or the density d_x, instead of M_x.

Thus, for the determination of the soundness of crystals a definite N_0 is needed, which in turn can be found using a substance with a *sound lattice* to make the necessary measurements. It is herewith proposed to regard *purest calcite crystals* as being such a substance, because of the following reasons:

(1) The growth of calcite occured only very slowly during long periods and its lattice should be perfect.

(2) Siegbahn obtained the sharpest x-ray spectral lines only with calcite crystals; this serves as an indication of the perfection of the lattice for the best calcite samples.

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[1] R. T. Birge, Phys. Rev. **62**, 301 (1942); U. Stille, Z. Physik **121**, 142 (1943); **125**, 174 (1948).

[2] See, for instance, F. Seith, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), pp. 3–76.

[3] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950); F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

[4] M. E. Straumanis, Acta Cryst. **2**, 83 (1949).

TABLE I. The absolute value of Avogadro's constant (physical scale).

	N_0
Du Mond and Cohen (1948)[a]	6.02514×10^{23}
The author (1949)[b, c]	6.02567
Bearden and Watts (1951)[d]	6.02566
Du Mond and Cohen (1952)[e]	6.02544
Stille (1952)[f]	6.02533

[a] See reference 15.
[b] See reference 4.
[c] See reference 13.
[d] See reference 16.
[e] See reference 14.
[f] See reference 17.

(3) Siegbahn's Avogadro constant (N_s) is related to all x-ray wavelength measurements,[5] which in turn, if multiplied by the conversion factor $\lambda_g/\lambda_c=1.00202$, agree perfectly with wavelength measurements made by means of gratings.[6]

(4) $N_{\text{universal}}$ (see Table I, DuMond and Cohen) agrees within the experimental error with N_0 determined from calcite, as shown below.

There also are disadvantages, since even the purest calcite samples contain some impurities in solid solution with the parent crystal,[7] and this changes the molecular weight of the substance.[8] Nevertheless, accurate determinations of N_0 are possible, if thorough analysis of the calcite (for the calculation of M) and precision determinations of lattice parameters and of density are made with the same samples.

However, it is also possible to calculate N_0 using the data already available. Siegbahn's Avogadro number ($N_s=6.0594\times10^{23}$ mole^{-1}),[5] obtained with the molecular weight of $\text{CaCO}_3=100.075$, can be easily corrected using the molecular weight for purest calcite (a mixed crystal), and the absolute wavelength in A.

N_0 calculated by means of Eq. (1) is

$$N_0=nM(\text{calcite})/dv, \tag{2}$$

where the volume of the unit cell v is expressed in A$^3/10^{24}$. N_s was obtained, and can be checked, by expressing the volume of the unit cell in kX$^3/10^{24}$ (1 kX is 1000X units), and using the above-mentioned molecular weight for CaCO_3:[5]

$$N_s=nM(\text{CaCO}_3)/dv'. \tag{3}$$

Assuming that the lattice of calcite is sound (in the sense mentioned above) and that the densities of purest calcite agree within the error limits with that used by Siegbahn, it is easily obtained from (2) and (3) that

$$N_0=\frac{M(\text{calcite})}{M(\text{CaCO}_3)}\frac{v'}{v}N_s=\frac{kN_s}{(1.00202)^3}, \tag{4}$$

because $v'/v=1/(1.00202)^3$. The latter is the conversion factor obtained by comparing the x-ray wavelengths, as measured by means of a grating and by the calcite crystal.[9]

The factor $k=100.095/100.075=1.00020\pm0.00003$ was previously determined by the author in 1944, and its necessity emphasized for determinations of x-ray molecular weight and Avogadro's number.[8,10] However, the respective papers, because of the war, did not appear in print until 1949, although they were accepted for printing in October, 1944. A paper by Birge, suggesting the same correction for Avogadro's number because of solid solution formation, appeared in 1945.[11]

If one considers only the change in the atomic weights of Ca and C since the time of Siegbahn's measurements, a value of $100.090/100.075=1.000149$ could be obtained. On the basis of the analysis of purest calcite samples,[12] a molecular weight of 100.095 was calculated for calcite, and the factor k then became 1.0002. Substituted for k in Eq. (4) the absolute Avogadro's number is[4,13]

$$N_0=(6.02403\pm0.00025)\times10^{23}\text{ g mole}^{-1}\text{ (chem.)},$$
$$N_0=(6.02567\pm0.00026)\times10^{23}\text{ g mole}^{-1}\text{ (phys.)}.$$

The relative error was computed assuming that $\Delta k=3\times10^{-5}\ k$, $\Delta(\lambda_g/\lambda_c)=1.1\times10^{-5}(\lambda_g/\lambda_c)$,[14] and $\Delta r=0.5\times10^{-5}\ r$, Δr being the error for the Smythe factor.[14] The systematic error, which is caused by the imperfections which still may be present in the crystals, is of course not known.

The reciprocal value of N_0 is 1.66002×10^{-24} (chem. scale) and not 1.66035×10^{-24} as derived from the old $N=6.02282\times10^{23}$. Calculated densities d_x then are given by the relation

$$d_x=1.66002\ nM_{\text{chem}}/v,$$

with v in A^3. Thus, the density value of purest calcite appears as a reference value.

Table I shows the agreement of N_0 (in the physical scale) with the evaluation of Avogadro's number by some other investigators.[4,13–17] These figures show that the value of N_0, derived from measurements made with purest calcite, is in excellent agreement with other evaluations, especially with those made by Bearden and Watts. It agrees also with the universal constant as calculated by the method of DuMond and Cohen, confirming the assumption of the soundness of the calcite lattice.

The proposition of regarding calcite as a reference substance with a lattice nearest to a sound one is therefore justified, and the perfection of lattices of other crystalline substances can now be compared with that

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[5] M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (J. Springer, Berlin, 1931), second edition, p. 43.

[6] K. Lonsdale, Acta Cryst. **3**, 400 (1950); W. L. Bragg, J. Sci. Instr. **24**, 27 (1947).

[7] A. Ieviņš and M. Straumanis, Z. Physik **116**, 194 (1940); see also K. W. Andrews, Mineralog. Mag. **29**, 85 (1950).

[8] M. Straumanis, Z. Physik **126**, 49, 60 (1949).

[9] J. A. Bearden, J. Appl. Phys. **12**, 395 (1941).

[10] M. Straumanis, Z. Physik **126**, 65 (1949).

[11] R. T. Birge, Am. J. Phys. **13**, 67 (1945).

[12] M. Straumanis and A. Dravnieks, Z. anal. Chem. **120**, 168 (1940).

[13] M. E. Straumanis, J. Appl. Phys. **20**, 726, 733 (1949).

[14] J. W. M. DuMond and E. R. Cohen, Am. Scientist **40**, 447, 450, 458 (1952).

[15] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **20**, 82 (1948).

[16] J. A. Bearden and H. M. Watts, Phys. Rev. **81**, 73 (1951).

[17] U. Stille, Physik. Bl. **8**, 397, 403 (1952).

one of calcite, using the value for N_0 as derived in the foregoing.

Note added in proof:—The new value for λ_g/λ_c recently calculated by DuMond and Cohen[18] is 1.002063. Substituting this value for 1.00202 in Eq. (4), $N_0 = 6.02489 \times 10^{23}$ (physical scale) is obtained, which is even in a better agreement with 6.02472×10^{23}, the newest $N_{\text{universal}}$ of the two authors,[18] than those of Table I. But if one uses the newest N_0, the respective λ_g/λ_c also must be used.

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[18] J. W. M. DuMond and E. Cohen, Revs. Modern Phys. 25, 691, 706 (1953).

PHYSICAL REVIEW VOLUME 92, NUMBER 5 DECEMBER 1, 1953

The Binary Rearrangement Collision*

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(Received July 3, 1953)

The theory of the general binary collision is discussed, and it is demonstrated that the rearrangement scattered amplitude can be derived from the integral equation which is convenient for determining the direct (no rearrangement of particles) scattered amplitudes. As a consequence, it is shown that no ambiguity in matrix element for the rearrangement amplitude in Born approximation exists.

THE binary rearrangement collision is a process in which a system A in state n collides with a system B in the state m, and systems C in state s and D in state t emerge. We shall consider events in which no photons are involved and that no particles appear or disappear. In previous treatments[1,2] of the general two-body collision different unperturbed Hamiltonians are employed for developing the stationary state integral equations. If no rearrangement of particles occurs in the collision, the relevant unperturbed Hamiltonian is that describing the relative motion of the two noninteracting systems A and B. If a rearrangement of particles occurs so that systems C and D appear, then it is convenient to select as unperturbed Hamiltonian that pertaining to the relative motion of C and D as noninteracting systems. However, with the latter procedure it is not clear from the derived integral equation in what way the boundary conditions are met since the incident wave, which is an eigenfunction of the alternative unperturbed Hamiltonian referring to systems A and B, is manifestly not present. Indeed, it is not apparent that the corresponding integral equations resulting from the separate imposition of the outgoing boundary condition describe the same wave function. Clearly, a single integral equation satisfying the boundary conditions should provide the amplitudes pertinent to any event, rearrangement or otherwise. It is the purpose of this note to demonstrate that this is indeed the case, and incidently to remove the serious ambiguity in matrix element arising in the Born approximation for rearrangement amplitudes. This ambiguity stems from the fact that either of the interaction energy operators between systems A and B, or C and D, yield the same matrix element[2] when exact wave functions for the unperturbed systems are presumed. However, such wave functions do not exist except in the very special three-body collision of electrons with hydrogen atoms, so that, in general, a difference in matrix element necessarily arises. For rearrangement (exchange) scattering of electrons from atoms this ambiguity has been referred to as "prior-post discrepancy,"[3,4] and has been clarified by an analysis[5] which will now be extended to the general binary collision.

We wish to solve the wave equation

$$(H-E)\Psi = 0, \tag{1}$$

where the Hamiltonian can be written in either of two ways,

$$H = H_{AB} + V_{AB} = H_{CD} + V_{CD}. \tag{2}$$

Since the entire calculation is performed in the center-of-mass system, the unperturbed Hamiltonians for the initial and final systems may be written as

$$H_{AB} = H_A(\mathbf{r}_a) + H_A(\mathbf{r}_b) - \frac{\hbar^2}{2\mu_{AB}} \nabla_{\mathbf{r}_{ab}}{}^2,$$

$$H_{CD} = H_C(\mathbf{r}_c) + H_D(\mathbf{r}_d) - \frac{\hbar^2}{2\mu_{CD}} \nabla_{\mathbf{r}_{cd}}{}^2.$$

Here $\mathbf{r}_a$, $\mathbf{r}_b$, $\mathbf{r}_c$, and $\mathbf{r}_d$ are the internal coordinates of the respective systems, while $\mathbf{r}_{ab}$ and $\mathbf{r}_{cd}$ denote the vectors that connect the centers of mass of the systems A, B and C, D respectively. For the internal motion we

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[*] The research reported in this paper has been sponsored by the Geophysical Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command.

[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1949), second edition.

[2] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 230.

[3] Bates, Fundaminsky, and Massey, Trans. Roy. Soc. (London) 243, 93 (1950).

[4] Corinaldesi, Trainor, and Wu, Nuovo cimento 9, 436 (1952).

[5] S. Altshuler, Phys. Rev. 91, 1167 (1953).