

LETTERS TO THE EDITORS

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Atomic Mass of Silicon

As is well known, the atomic mass of silicon has not yet been determined with satisfactory accuracy. The value given in the International Table of Atomic Weights is 28.06. Practically the same value, 28.063, was given by Baxter, Weatherill and Scripture¹ in 1923 from the ratio $\text{SiCl}_4/4\text{Ag}$. But from the same ratio, figures of 28.11, had been obtained in 1920 by Baxter, Weatherill and Holmes² and of 28.10₅ by Hönigschmidt and Steinheil³. Finally, in 1923, Weatherill and Brundage⁴, from the ratio $\text{SiCl}_4/\text{SiO}_2$, gave the value 28.10₆. The three of the four modern gravimetric values are in fair agreement and lead to a mean figure of 28.10₆, which exceeds by 1/610 approximately the figure given in the International Table. This difference, considering the precision of modern gravimetric methods, is too great to be accepted without reservations, and it makes desirable and urgent a further revision of the atomic mass of silicon.

For this reason the recent publication of the experiments carried out by E. P. Ney and McQueen⁵ with the mass-spectrograph on the isotopes of silicon must be welcomed. Subjecting silicon fluoride to an electronic bombardment, several ions are produced, among which the group SiF^+ is particularly interesting, from which it was possible to measure the mass and the abundance of the three isotopes, ²⁸Si (92.24 ± 0.10); ²⁹Si (4.69 ± 0.05) and ³⁰Si (3.07 ± 0.05). From these data, Ney and McQueen give the value of the atomic mass of silicon as 28.087, exceeding by 1/1039 the figure accepted by the International Commission.

The revision of the atomic mass of silicon has been undertaken at the Laboratory of Physical Chemistry of Compostela (Spain) using the pykno-X-ray method. This method, applied for the first time by Hutchison and Johnston to the determination of the atomic mass of fluorine⁶, is based on the comparison of the molecular mass of the substance with that of calcite. The molecular mass of a crystal depends on: (a) the volume of its unit cell; (b) the number of molecules contained in the latter; (c) its density (ρ); and (d) Avogadro's number (N_A); hence when these values are known—at a given temperature—for the substance and the calcite, a simple formula enables the atomic mass to be calculated.

The compound chosen for the revision of the atomic mass of silicon was silica (SiO_2), in the form of α -quartz of hexagonal structure, the X-ray constants of which accurately determined by A. H. Jay⁷ at 18° C. are: $a = 4.9029 \text{ \AA}$, and $c = 5.3933 \text{ \AA}$. As regards density, the pykno-metric measurements at 0° C., carried out by C. Gutierrez Losa in this Laboratory using our precision technique⁸ with very pure transparent quartz from Noya (Corunna, Spain) give the mean value: $\rho_0^0 = (2.6506_8 \pm 0.0002_3) \text{ gm./cm.}^3$. Taking as coefficient of cubic expansion of α -quartz⁹ the value 3.529×10^{-5} , the density of SiO_2 at 18° C. will be: $\rho_0^{18} = (2.6490_0 \pm 0.0002_3) \text{ gm./cm.}^3$. As regards calcite, I have taken as molecular mass, $M_{\text{CaCO}_3} = 100.090$, and as density, grating space and geometric structural constant, $\varphi(\beta)$, at 18° C., the values given by Bearden and Bearden and Shaw¹⁰:

$\rho_0^{18} = 2.71036 \text{ gm./cm.}^3$, $d^{18} = 3.02945 \text{ \AA}$, and $\varphi(\beta) = 1.09598$.

From the equations,

$$M_{\text{SiO}_2} = \frac{\sqrt{3}}{6} \cdot N_A \cdot \rho_{\text{SiO}_2} \cdot a^2 \cdot c$$

and

$$M_{\text{CaCO}_3} = 2 \cdot N_A \cdot \rho_{\text{CaCO}_3} \cdot \varphi(\beta) \cdot d^3_{\text{CaCO}_3}$$

and expressing the molecular mass of SiO_2 and CaCO_3 as a function of the other magnitudes mentioned, we conclude

$$M_{\text{SiO}_2} = M_{\text{CaCO}_3} \cdot \frac{\sqrt{3}}{12} \cdot \frac{\rho_{\text{SiO}_2}}{\rho_{\text{CaCO}_3}} \cdot \frac{a^2 \cdot c}{\varphi(\beta) \cdot d^3_{\text{CaCO}_3}}$$

Substituting in this equation the various numerical values, we find $M_{\text{SiO}_2} = 60.075$, the atomic mass of silicon being, therefore,

$$\text{Si} = 28.075.$$

This determination is based on the molecular mass of calcite. This may not be the best reference substance for our purpose, since "it is well known to crystallographers that calcite always contains impurities"¹¹, and also because in the value of its molecular mass there is an approximate error of ± 0.007. On this account it is advisable, in my opinion, to take as reference substance sodium chloride, the molecular mass, density and grating space of which have been accurately determined. From

$$M_{\text{NaCl}} = 2N_A \cdot \rho_{\text{NaCl}} \cdot d^3_{\text{NaCl}}$$

it can be deduced that

$$M_{\text{SiO}_2} = M_{\text{NaCl}} \cdot \frac{\sqrt{3}}{12} \cdot \frac{\rho_{\text{SiO}_2}}{\rho_{\text{NaCl}}} \cdot \frac{a^2 \cdot c}{d^3_{\text{NaCl}}}$$

Taking as molecular mass, $M_{\text{NaCl}} = 58.454$, as density, at 18° C., the figure given by Johnston and Hutchison¹², $\rho_0^{18} = 2.16396 \text{ gm./cm.}^3$, and as grating space, $d^{18} = 2.81425 \text{ \AA}$, and substituting these figures in the above equation, we obtain $M_{\text{SiO}_2} = 60.076$, or $\text{Si} = 28.076$, in good agreement with the figure obtained taking calcite as reference. The mean value of the two atomic masses thus found,

$$\text{Si} = 28.075,$$

is somewhat lower than the value found by Ney and McQueen, but higher than the one accepted by the International Commission. The most recent determinations seem, therefore, to suggest that the atomic mass of silicon is slightly higher than the one still given in the International Table.

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March 7.

¹ Baxter, Weatherill and Scripture, *Proc. Amer. Acad. Sci.*, **58**, 245 (1923).

² Baxter, Weatherill and Holmes, *J. Amer. Chem. Soc.*, **42**, 1194 (1920).

³ Hönigschmidt and Steinheil, *Z. anorg. Chem.*, **141**, 101 (1924).

⁴ Weatherill and Brundage, *J. Amer. Chem. Soc.*, **54**, 3932 (1932).

⁵ Ney, E. P., and McQueen, *Phys. Rev.*, **69**, 41 (1946).

⁶ Hutchison, C. A., and Johnston, H. L., *J. Amer. Chem. Soc.*, **63**, 1580 (1941).

⁷ Jay, A. H., *Proc. Roy. Soc. Lond.*, **A**, **142**, 237 (1933).

⁸ Batuecas, T., and Casado, F. L., *J. Chim. phys.*, **33**, 41 (1936); *Z. phys. Chem.*, **A**, **181**, 197 (1938); *Bol. Univ. Santiago de Compostela* (Oct.-Dec., 1935).

⁹ "International Crit. Tab.", **4**, 21 (1928).

¹⁰ Bearden, *Phys. Rev.*, **36**, 2089 (1931). Bearden and Shaw, *Phys. Rev.*, **48**, 18 (1935).

¹¹ Birge, E. T., *Amer. J. Phys.*, **13**, 70 (1945).

¹² Johnston, H. L., and Hutchison, C. A., *Phys. Rev.*, **62**, 32 (1942).