

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON THERMODYNAMICS AND
THERMOCHEMISTRY†
COMMISSION ON DATA AND STANDARDS
VALUES OF THE FUNDAMENTAL CONSTANTS
FOR CHEMISTRY

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The progress of science throughout the world requires that there be an adequate system of communication among scientists. Scientists have to communicate a tremendous amount of information, much of which is quantitative in character. The transmission of quantitative information should be made without the introduction of extraneous errors arising from the use by different investigators of discordant values of the fundamental constants.

An experimental scientist makes measurements in his laboratory of certain physical phenomena, with instruments and apparatus calibrated in terms of the fundamental units of measurement—length, mass, and time. Most frequently, this investigator reports in the literature quantitative information which is not precisely alone the quantities he has measured, but these combined with certain fundamental constants to obtain quantities for comparison with related observations of other investigators. It is important, therefore, that the values of such fundamental constants be ones generally accepted by the scientific community.

For proper and convenient communication, without misunderstanding, different investigators must use the same values of the fundamental constants in reducing their respective data, otherwise, the reported quantities may be significantly different even though the quantities originally measured may actually have been in complete accord. It is important, therefore, for all of science, that we have continually available a currently acceptable self-consistent set of "best" values of the fundamental constants.

The need for fundamental constants was recognized in chemistry many years ago when there was established the chemists' international scale of atomic weights, so that chemists throughout the world might communicate their observations in a quantitative language readily understood by all scientists. In addition to a self-consistent set of values for the atomic weights,

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the science of chemistry needs also a self-consistent set of "best" values of the fundamental constants. This need is particularly strong in the communication of quantitative information on the physical, thermodynamic, spectral, and other properties of the chemical substances.

When Volume I of the International Critical Tables¹ appeared in 1926, it carried a complete list of recommended values of the fundamental constants. Within a few years, the important publications of Birge²⁻⁴ appeared in 1929, 1941, and 1945, showing the need for very significant changes in the values of certain constants. In the period 1937 to 1939, reports on fundamental constants were published by von Friesen⁵, Dunnington⁶, and Wensel⁷. In 1948, a report on fundamental constants by Stille⁸ appeared. In 1951, Bearden and Watts⁹ published a recommended set of fundamental constants. In 1948 and 1951, Du Mond and Cohen^{10, 11} published a very extensive and thoroughly documented set of fundamental constants. Within the respective limits of uncertainty, the values from these last two investigations were in substantial accord. Although somewhat different, each set was self-consistent. The set of constants from the 1951 report of Du Mond and Cohen¹¹ served as the basis for the report of the National Research Council, U.S.A., on the status of the values of the fundamental constants for physical chemistry as of July 1, 1951, which report was published¹² in 1952. In 1955, Cohen, Du Mond, Layton, and Rollett¹³ issued another complete adjustment of the values of the fundamental constants. In the period 1954 to 1959, reports on fundamental constants were published by Bearden, Earle, Minkowski, and Thomsen¹⁴ and by Bearden and Thomsen^{15, 16}.

Meanwhile, in 1955, the Advisory Committee on Thermometry of the International Committee on Weights and Measures had obtained international approval for the definition of the absolute temperature of the triple point of water as exactly 273.16 °K. Since the temperature of the conventional "ice point" is lower¹⁷ by 0.0100 ± 0.0001 °C, the absolute temperature of the ice point thus became 273.1500 ± 0.0001 °K. Prior to this time, the absolute temperature of the ice point had been obtained from experimental measurements, involving, directly or indirectly, the pressure-volume product for one mole of a gas at zero pressure, at the ice point (0°C) and at the steam point (100°C). In most of the sets of values of the fundamental constants referred to above, the value of the absolute temperature of the ice point had been selected as 273.160 ± 0.010 °K. Thus, a very significant change in this constant was introduced, particularly for thermodynamic quantities, since the value of the gas constant R is obtained as the quotient of the pressure-volume product for one mole of gas at zero pressure and 0°C, divided by the absolute temperature of the ice point:

$$R = (PV)_{0^{\circ}\text{C}}^P / T_{0^{\circ}\text{C}} \quad (1)$$

Then in 1960 and 1961 came the unification of the chemists' and the physicists' scales of atomic weights, by action of the International Union of Pure and Applied Physics (I.U.P.A.P.) and the International Union of Pure and Applied Chemistry (I.U.P.A.C.). The former chemists' scale was based on one mole as 16 grams of naturally occurring oxygen, containing ¹⁶O, ¹⁷O, and ¹⁸O. The former physicists' scale was based on one mole as

16 grams of pure ^{16}O . The new scale of atomic weights is based on one mole as 12 grams of pure ^{12}C . To attain the new unified scale, the former chemists' values were decreased by 43 parts per million and the former physicists' values were decreased by 318 parts per million¹⁸⁻²¹.

For thermodynamicists interested in the value of the gas constant R , the change in the absolute temperature of the ice point from 273.16 to 273.15 (a decrease of 37 parts per million in $T_0^\circ\text{C}$) and the change in the scale of atomic weights (a decrease of 43 parts per million in the size of one mole) almost cancelled one another (see equation 1), leaving a net change of only -6 parts per million, a negligible amount.

The foregoing changes in the absolute temperature of the ice point and in the scale of atomic weights, along with the appearance of much new experimental data relating to the atomic constants, resulted in new adjustments of the values of the fundamental constants by Cohen and Du Mond²² and by Bearden and Thomsen²³. Early in 1963, the National Research Council (U.S.A.) Committee on Fundamental Constants† approved a recommended set of values of the fundamental constants based on the latest work of Cohen and Du Mond, with suggestions by Bearden and Thomsen.

At the 1963 Conference of the International Union of Pure and Applied Chemistry in London, in early July, the foregoing recommended set of fundamental constants was brought to the attention of the Commission on Thermodynamics and Thermochemistry and the Commission on Physico-chemical Data and Standards. Both Commissions were in favour of having an internationally agreed-upon set of fundamental constants, and, at their suggestion, the Secretary-General of I.U.P.A.C., Dr Rudolf Morf, requested the writer, then Associate Member of the I.U.P.A.C. Commission on Thermodynamics and Thermochemistry, and Chairman of its Task Group on Fundamental Constants, to represent I.U.P.A.C. at the Second International Conference on Nuclidic Masses at Vienna, July 15-19, 1963, and to attend the meeting there of the Commission on Nuclidic Masses and Related Atomic Constants of I.U.P.A.P.

At the Second International Conference on Nuclidic Masses, (J. H. E. Mattauch, President), Cohen²⁴ presented a paper entitled "1963 Status Report on the Fundamental Constants". At the same Conference, the writer²⁵ presented a report entitled "The International Union of Pure and Applied Chemistry and its Interest in the Values of the Fundamental Constants", stating that I.U.P.A.C. was anxious to reach accord with I.U.P.A.P. on the use of a single, self-consistent set of fundamental constants, citing the adoption of the ^{12}C unified scale of atomic weights as an outstanding example of the fruits of co-operation, and indicating that the appropriate groups belonging to I.U.P.A.C. had reviewed the Cohen-Du Mond set of constants and were prepared to recommend their use by chemists as "best" values, with the understanding that they would be subject to revision at appropriate intervals by the proper authorities.

At the meeting of the I.U.P.A.P. Commission on Nuclidic Masses and Related Atomic Constants during the same Conference, Cohen and Du Mond presented their report on "Recommended values of the Physical

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Constants—1963". The views of I.U.P.A.C. on fundamental constants were also brought before this Commission by the writer²⁵.

The I.U.P.A.P. Commission on Nuclidic Masses and Related Atomic Constants then approved the following resolution for presentation to the General Assembly of the International Union of Pure and Applied Physics at Warsaw later in 1963:

"The Commission of Nuclidic Masses and Related Atomic Constants has encouraged two of its members, J. W. M. Du Mond and E. R. Cohen, to prepare a self-consistent list of the most probable values of the fundamental constants. This list was presented to the Second International Conference on Nuclidic Masses held in Vienna, July 15–19, 1963. The Commission expects that these values will be widely used and will help to remove many of the confusions that have arisen from the use of differing sets of constants. In addition, it is expected that the appearance of this list will encourage further experimental work aimed at improving our knowledge of these values."

This resolution was approved by the 1963 General Assembly of I.U.P.A.P.

The recommended values of the fundamental constants presented in the 1963 Cohen–Du Mond report, as received by the National Research Council (U.S.A.)²⁶, by the I.U.P.A.P. Commission on Nuclidic Masses and Related Atomic Constants, and by the I.U.P.A.C. Commissions on Thermodynamics and Thermochemistry and Physico-chemical Data and Standards, are presented in this report in a somewhat different arrangement.

Before proceeding to the values of the fundamental constants, we may usefully note the fundamental units in terms of which all measurements are made—length, mass, and time, as presently approved by the International Committee on Weights and Measures:

The unit of length is the *metre*, represented by the symbol *m*, which is equal to 1,650,763.73 wavelengths of light *in vacuo* produced by the unperturbed transition $2p_{10}-5d_5$ in ^{86}Kr .

The unit of mass is the *kilogram*, represented by the symbol *kg*, which is equal to the mass of the international kilogram maintained at the International Bureau of Weights and Measures at *Sevres*, near Paris, France.

The unit of time is the second, represented by the symbol *s*, which is equal to $1/(31,556,925.9747)$ of the tropical year at 12^h ET, 0 January, 1900.

For a better appreciation of the relative importance of the various fundamental constants, and their relations one to another, it is convenient to classify them arbitrarily into three categories: (i) the defined constants, the values of which are fixed exactly by definition; (ii) the basic constants, the values of which are, in the main, obtained from experimental measurements in terms of the fundamental units of length, mass, and time; and (iii) the derived constants, the values of which are, in the main, obtained from the foregoing two categories and appropriate physical relations.

The values of the defined constants are given in *Table 1*.

In connection with the defined value for the absolute temperature of the triple point of water given in *Table 1*; the following should be noted¹⁷: Experimental data show the difference between the triple point of water (temperature of equilibrium of solid, liquid, and gaseous water) and the so-called "ice point" (temperature of equilibrium of solid and liquid water

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Table 1. Values of the "defined" constants

Constant	Symbol	Value (exact, by definition)
Unified atomic mass unit	<i>u</i>	1/12 times the mass of an atom of ¹² C
Mole	mol	The amount of a substance, of specified chemical formula, containing the same number of formula units (molecules, atoms, ions, electrons, or other entities) as there are atoms in 12g (exactly) of the pure nuclide ¹² C
Standard acceleration of gravity, in free fall	<i>g</i>	980.665 cm s ⁻²
Normal atmosphere, pressure	atm	1,013,250 dyn cm ⁻²
Absolute temperature of the triple point of water†	<i>T</i> _{tp}	273.16°K
Thermochemical calorie	cal	4.184 J
International steam calorie	cal _{IT}	4.1868 J
Inch	in.	2.54 cm
Pound, avoirdupois	lb.	453.59237 g

† The difference between the temperature of the triple point of water and the so-called "ice point" (temperature of equilibrium of solid and liquid water saturated with air at one atmosphere) is accurately known¹⁷: $T(\text{triple point}) - T(\text{ice point}) = 0.0100 \pm 0.0001$ °K.

saturated with air at a pressure of 1 atmosphere) to be T (triple point) — T (ice point) = 0.0100 ± 0.0001 °C. On the advice of its Advisory Committee on Thermometry, the (International) General Conference on Weights and Measures adopted the following resolution in 1948: "With the present day technique, the triple point of water is susceptible of being a more precise thermometric reference point than the melting point of ice. The Advisory Committee considers, therefore, that the zero of the thermodynamic Celsius scale should be defined as being the temperature 0.0100° below that of the triple point of pure water".

Given values for five of the basic fundamental constants, we have all the values needed for chemistry, since with these five and the defined constants, together with the appropriate physical relations, we can derive the values of all the other constants needed. Actually, no five basic constants are uniquely determined accurately enough by themselves alone. As explained in the reports of Cohen and Du Mond^{22, 24}, their elaborate least-squares adjustment was based on eleven primitive experimental input data subject to adjustment with seven accurately known auxiliary constants, taken as fixed, to yield values for four constants, the Sommerfeld five structure constant, the electronic charge, Avogadro's number, and the factor for converting X-ray measurements of length.

From the tabulation of values of the constants given by Cohen and Du Mond, we can arbitrarily select the following five and label them as "basic" constants: the velocity of light, c ; Avogadro's number, N ; Faraday's constant, F ; Planck's constant, h ; and the pressure-volume product of one mole of a gas at 0°C and zero pressure, $(PV)_{0^\circ\text{C}}^{P=0}$.

Given values for these five constants, it is possible to utilize appropriate physical relations and the defined constants to obtain values for all the other needed constants. For example: the charge on the electron, $e = F/N$; the gas constant per mole, $R = (PV)_{0^\circ\text{C}}^{P=0}/T_{0^\circ\text{C}}$; Boltzmann's constant, $k = R/N$; the second radiation constant, $c_2 = hc/k$; the constant relating

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mass and energy, $Y = c^2$; and the constant relating wavenumber and energy, $Z = Nhc$.

Table 2 gives the recommended values for these arbitrarily selected five "basic" constants.

Table 2. Recommended values of the "basic" constants†

Constant	Symbol	Value (with estimated uncertainty)
Velocity of light in <i>vacuo</i>	c	2.997925×10^{10} cm s ⁻¹ ±0.000003
Avogadro number	N	6.02252×10^{23} molecules mol ⁻¹ ±0.00028
Faraday constant	F	96,487.0 coulomb equiv ⁻¹ ±1.6 23,060.9 cal volt ⁻¹ equiv ⁻¹ ±0.4
Planck constant	h	6.6256×10^{-27} erg s ±0.0005
Pressure-volume product for one mole of gas at 0°C and zero pressure	$(PV)_{0^\circ\text{C}}^{P=0}$	2271.06 J mol ⁻¹ ±0.12 22413.6 cm ³ atm mol ⁻¹ ±1.2

† The selection of these constants as the five "basic" ones is somewhat arbitrary. A least squares adjustment such as that of Cohen and Du Mond actually treats, on an equal basis, both the "basic" constants and those "derived" constants which can be evaluated experimentally. In order to evaluate the accuracy of any constant derived from those on this list it is necessary to use the complete error matrix as more fully explained in the report of Cohen and Du Mond.

Table 3 gives the recommended values of the "derived" constants useful in chemistry, using appropriate values given in Tables 1 and 2.

The reports of Cohen and Du Mond may be referred to for details regarding the evaluation of the atomic constants. The uncertainties assigned to the values for $(PV)_{0^\circ\text{C}}^{P=0}$, R , k , Z , and c_2 in Tables 2 and 3 of this report are somewhat less than those given by Cohen and Du Mond, and have been

Table 3. Recommended values of the "derived" constants

Constant	Symbol and relation	Value (with estimated uncertainty)
Elementary charge	$e = F/N$	4.80298×10^{-10} cm ^{3/2} g ^{1/2} s ⁻¹ (esu) ±0.00020
Gas constant	$R = (PV)_{0^\circ\text{C}}^{P=0}/T_{0^\circ\text{C}}$	8.31433 J deg ⁻¹ mol ⁻¹ ±0.00044 1.98717 cal deg ⁻¹ mol ⁻¹ ±0.00011
Boltzmann constant	$k = R/N$	1.38054×10^{-16} erg deg ⁻¹ molecule ⁻¹ ±0.00009
Second radiation constant	$c_2 = hc/k$	1.43879 cm deg ±0.00009
Einstein constant relating mass and energy	$Y = c^2$	8.987554 × 10 ¹³ J g ⁻¹ ±0.000018 2.148076 × 10 ¹³ cal g ⁻¹ ±0.000004
Constant relating wave number and energy	$Z = Nhc$	11.96255 J cm mol ⁻¹ ±0.00038 2.85912 cal cm mol ⁻¹ ±0.00009

made consistent with their complete error matrix. Also, the value of the constant R is given to one more significant figure. The report of Cohen and Du Mond gives values for many more "derived" constants than those given in *Table 3* here.

It is expected that the appropriate bodies will continue their study and scrutiny of the values of the fundamental constants, so that revisions may be made at suitable intervals by the proper authorities.

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