solutions over a range in concentration of 0.18–0.82 *M* cupric salt in the first group of solutions and 0.22–0.67 *M* in the second.

2. By means of an electromotive-force method for the determination of the necessary ion activities, evidence for the univalence of the cuprous ion was found and the following molal electrode potentials at 25° were calculated: Cu, Cu^+, —0.522 volt; and Cu^+, Cu^{++}, —0.167 volt.

3. From the foregoing data the equilibrium constant $K_1 = [Cu^{++}]/[Cu^+]^2$ was found to be 1×10^6, with a mean deviation of 10%.

4. The electromotive force of the cell, $H_2 \mid HClO_4 \mid HClO_4 + Hg_2(ClO_4)_2 \mid Hg$, was measured and the ratio of the square of the activity coefficient of hydrogen ion to the activity coefficient of mercurous ion calculated over a range in ionic strength of 0.16–4.17.

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[CONTRIBUTION FROM THE NELA RESEARCH LABORATORY]

A SIMPLE RELATION BETWEEN COMPOSITION AND BOILING POINT[1]

BY ELLIOT Q. ADAMS

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Of the equations for the approximate calculation of boiling points of normal organic liquids, perhaps the best known is that of Longuinesu[2]

$$T/(D\sqrt{n}) \doteqdot 100 \qquad (1)$$

in which *T* is the absolute boiling point (°K.); *D*, the density of the liquid, and *n*, the number of atoms in the molecule.

It seems worth while to call attention to an even simpler expression

$$T \doteqdot \sqrt{20{,}000\, m} \qquad (2)$$

which holds within a fraction of a unit in m for most normal[3] *organic* liquids and many inorganic non-electrolytes.

T is, as before, the absolute boiling point at 760 mm. pressure; *m* is, in the case of hydrocarbons, the number of carbon atoms in the molecule. For other elements, the number of atoms is to be multiplied by one less than the number of the row in the periodic system,[4] Fig. 1, in which the

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Washington, April, 1924. Equation 3 has been added in the rewriting.

[2] Longuinesu, *J. chim. phys.*, **1**, 288, 296, 391 (1903); **6**, 552 (1908).

[3] Compare J. H. Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, pp. 84, 91, 94. Normal organic liquids may be defined as those which do not contain hydrogen (or metallic elements) directly united to any element except carbon, which do not have intramolecular ionization (as in betaine), and which do not contain multiple bonds except between carbon atoms. This definition excludes esters, most of which appear to be normal.

[4] *J. H. Hildebrand, "Principles of Chemistry," The MacMillan Co., New York,* **1918**, p. 257. He credits the form of the table to J. Thomsen [*Z. anorg. Chem.*, **9**, 190–3 (1895)], although it has not a single feature that was original with Thomsen. Com-

element occurs. As an illustration, for cacodyl chloride, $(CH_3)_2AsCl$, $m = 2 + (6 \times 0) + (1 \times 3) + (1 \times 2) = 7$; $T = \sqrt{20{,}000 \times 7} = 374°K.$ or 101°C. The boiling point is stated to be $> 100°$.

If the boiling point is given, or desired, at some other pressure than 760 mm., the approximate relation[5]

$$T \doteq T_p\,(1 - 0.2 \log_{10} p) \qquad (3)$$

where T_p is the absolute boiling point at a pressure of p atmospheres, may be used to calculate T from T_p, or *vice versa.*

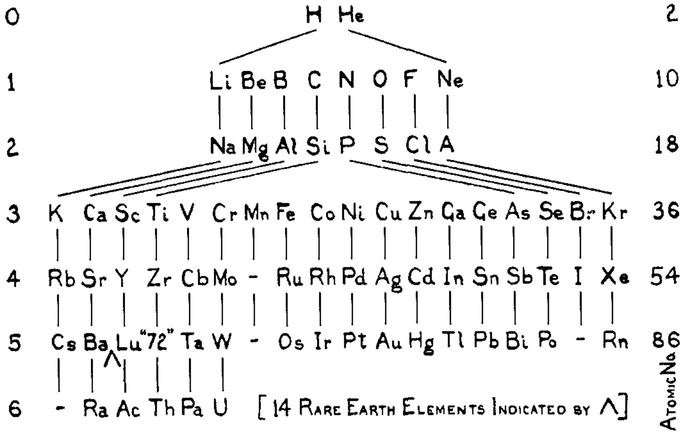

Fig. 1.

Table I compares values of m calculated by Equation 2—and if necessary Equation 3—with those deduced from the positions in the periodic system of the elements present. The boiling points are taken from the 1923 "Chemiker Kalender."

TABLE I

VALUES OF "m" FROM FORMULA OF COMPOUNDS AND FROM EQUATIONS 2 AND 3

Substance	Formula	B. p., °C.	Pressure, mm.	T, °K.	$m = T^2/20{,}000$	m from formula
n-Pentane	C_5H_{12}	36	760	309	4.8	5
n-Octylene	C_8H_{16}	123	760	396	7.8	8
Toluene	C_7H_8	111	760	384	7.4	7
n-Amyl iodide	$C_5H_{11}I$	155	760	428	9.1	9
Ethyl ether	$C_4H_{10}O$	35	760	308	4.7	5
Diethyl peroxide	$C_4H_{10}O_2$	65	760	338	5.7	6
Methylal	$C_3H_8O_2$	42	760	315	5.0	5
Ethyl acetate	$C_4H_8O_2$	77	760	350	6.1	6
Ethyl caprate	$C_{12}H_{24}O_2$	245	760	518	13.4	14
Triethylamine	$C_6H_{15}N$	89	760	362	6.5	7

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pare Bayley, *Phil. Mag.*, [5] **13,** 26 (1882). Stoney, *Chem. News*, **55,** 257 (1888); reprinted in *Phil. Mag.*, [6] **4,** 411 (1902). Werner, *Ber.*, **38,** 914 (1905). Adams, THIS JOURNAL, **33,** 684 (1911). Also Margary, *Phil. Mag.*, [6] **42,** 287–8 (1921).

[5] Obtained by combining Trouton's rule and the integrated Van't Hoff equation.

TABLE I (*Concluded*)

Substance	Formula	B. p., °C.	Pressure, mm.	T, °K.	$m = T^2/20{,}000$	m from formula
Triethylphosphine........	$C_6H_{15}P$	128	760	401	8.0	8
Cacodyl..................	$C_4H_{12}As_2$	170	760	443	9.8	10
Zinc methyl.............	C_2H_6Zn	46	760	319	5.1	5
Mercury ethyl...........	$C_4H_{10}Hg$	159	760	432	9.3	9
1,2,3,4-Tetrobromobutane.	$C_4H_6Br_4$	181	60	554	15.3	16
n-Octadecylene...........	$C_{18}H_{36}$	179	15	606	18.4	18
Bismuth triethyl.........	$C_6H_{15}Bi$	107	79	455	10.3	11
Carbon bisulfide..........	CS_2	46	760	319	5.1	5
Selenium tetrafluoride.....	SeF_4	100	760	373	6.9	7
Hydrogen telluride.......	H_2Te	0	760	273	3.7	4

Systematic deviations from Equation 2 are shown by some classes of presumably normal liquids: branched-chain, especially quaternary, hydrocarbons, and halogen derivatives with several halogen atoms attached to the same carbon atom, boil low; while cyclic compounds boil high.

Associated or polar liquids, as is well known, boil higher than would be expected from their nominal composition—the excess usually amounts to several units in m.

Summary

If T is the absolute boiling point at one atmosphere—or T_p the absolute boiling point at a pressure of p atmospheres—and m is the sum of the number of atoms of each element multiplied by one less than the number of the row of the periodic table in which it occurs, the relation

$$T \doteq T_p\,(1 - 0.2 \log_{10} p) \doteq \sqrt{20{,}000\ m} \qquad (2,3)$$

holds within a fraction of a unit of m for most normal organic liquids, and for many inorganic non-electrolytes.

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[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE CONSTITUTION OF NICKEL CARBONYL AND THE NATURE OF SECONDARY VALENCE

BY ARTHUR A. BLANCHARD AND WILLIAM L. GILLILAND

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In its ease of formation from and dissociation into metallic nickel and carbon monoxide, nickel carbonyl strongly resembles the hydrates of salts. Hydrate formation is usually ascribed to a "secondary" valence of the constituents of the salt whose "primary" valence has already been engaged.

In the case of nickel carbonyl, however, it would seem as if the secondary valence alone became engaged while the primary valences which both nickel and carbon monoxide are capable of developing remained dormant.