[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

An Explanation of Chemical Variations within Periodic Major Groups

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"Anomalous" chemical variations within periodic major groups are summarized and shown to be of general occurence. New electronegativity values of elements are presented as an aid to understanding such variations. In particular, the transition within a periodic group from an 8-shell to an 18-shell type of atom appears to be associated with an *increase* in electronegativity, which diminishes from left to right in the periodic table and disappears in the halogens.

Chemical variations and alterations within periodic major groups have long been recognized[1] but have usually been regarded as anomalous. In part this has been accepted as the inevitable result of the oversimplification inherent in any periodic table. Perhaps even more, the idea of anomaly has found support in the generally accepted belief that the chemical elements within any major group of the periodic table show a consistent, although non-uniform, trend of decreasing electronegativity with increasing atomic number. A recently proposed method[2] of evaluating electronegativities gives values which are in general agreement with the values of Pauling[3] and the similar values of Gordy[4] for the first twenty elements but, beyond these, show alternations which are not paralleled by the electronegativity values earlier accepted. It is the purpose of this paper (1) to summarize reported chemical evidence showing that alternations in properties within a major group are actually of quite general occurrence, and (2) to demonstrate that they are not necessarily anomalous, in the light of the new electronegativity values.

The general occurrence of chemical variations is illustrated by a number of examples in Table I. All of these variations appear anomalous if the elements of these groups consistently decrease in relative electronegativity with increasing atomic number.

The new method of evaluating electronegativities,[2] which utilizes a function of electronic density called the "stability ratio *(SR)*," gives electronegativities which alternate in the manner depicted in Fig. 1. In particular, the transition within a periodic group from an 8-shell to an 18-shell type of atom gives an *increase* in electronegativity, as evaluated by stability ratios. The difference diminishes in going from left to right across the periodic table, numerically being as follows: Ga–Al, 1.29; Ge–Si, 0.97; As–P, 0.57; Se–S, 0.14. The reason for the greater electronegativities of the 18-shell elements, according to the stability ratio theory, is that their atoms are more compact, and therefore have a correspondingly greater tendency to take on electrons, partially or wholly, by which process their electronic spheres expand toward greater stability.

TABLE I

SOME EXAMPLES OF CHEMICAL VARIATIONS

Group III:

(1) B_2H_6 and Ga_2H_6 volatile,[5] but $(AlH_3)_x$ non-volatile[6]
(2) Stable borohydride formed by Al[7] but not by B or Ga[8]
(3) $AlMe_3$ and $AlEt_3$ dimeric in vapor,[9,10] but B[11] and Ga[12] analogs monomeric
(4) $AlMe_3$ hydrolyzed rapidly and completely,[10,13] but BMe_3 not at all[14] and $GaMe_3$ only to Me_2GaOH in cold[12]

Group IV:

(5) Ge, more than Si, resembles C[15]
(6) SiH_4 much more readily oxidized and hydrolyzed[16] than CH_4 or GeH_4[17]
(7) Heats of formation: GeO_2 128, SiO_2 208 kcal./mole.[18] GeO_2, not SiO_2, reduced with H_2 at 540°[19]

Group V:

(8) PCl_5 and $SbCl_5$ known but not $AsCl_5$[20]
(9) N(V) and As(V) oxidizing agents, but not P(V)
(10) N(III) and As(III) much weaker reducing agents than P(III)
(11) $PCl_3 + AsF_3 \rightarrow PF_3 + AsCl_3$[21]
(12) $AsCl_3$ in nitrobenzene reduced by Sb, Bi and P[22]

Group VI:

(13) Se(IV and VI) stronger oxidizing agent than S(IV and VI)[23]
(14) Se(IV) more difficult to oxidize than S(IV)

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(1) (a) J. H. Hildebrand, *J. Chem. Ed.*, **18**, 291 (1941); Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1929, p. 167; 1940, p. 209; 1951, p. 217; (b) H. I. Schlesinger, "General Chemistry," 4th Ed., Longmans, Green and Co., New York, N. Y., 1950, p. 529.

(2) R. T. Sanderson, *Science*, **114**, 670 (1951); THIS JOURNAL, **74**, 272 (1952); *J. Chem. Phys.*, **20**, 535 (1952).

(3) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

(4) W. Gordy, *Phys. Rev.*, **69**, 604 (1946).

(5) E. Wiberg and T. Johannsen, *Naturwissenschaften*, **29**, 320 (1941).

(6) O. Stecher and E. Wiberg, *Ber.*, **75B**, 2003 (1942).

(7) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **61**, 536 (1939); **62**, 3421 (1940).

(8) H. I. Schlesinger, H. C. Brown and G. W. Schaeffer, *ibid.*, **65**, 1786 (1943).

(9) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941).

(10) K. S. Pitzer and H. S. Gutowsky, *ibid.*, **68**, 2204 (1946).

(11) A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921).

(12) (a) C. A. Kraus and F. E. Toonder, *Proc. Natl. Acad. Sci. U. S.*, **19**, 292 (1933); (b) Brandt, Thesis, Cornell University, 1932.

(13) G. B. Buckton and W. Odling, *Ann. Spl.*, **4**, 109 (1865).

(14) E. Frankland and B. F. Duppa, *Phil. Trans.*, **152**, 167 (1862); *Proc. Roy. Soc. (London)*, **25**, 165 (1876).

(15) A. Tchakirian, *Ann. chim.*, **12**, 415 (1939).

(16) A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

(17) H. J. Emeleus and E. R. Gardner, *J. Chem. Soc.*, 1900 (1938).

(18) R. Schwarz, *Die Chemie*, **55**, 43 (1942).

(19) L. M. Dennis, K. M. Tressler and F. E. Hance, THIS JOURNAL, **45**, 2034 (1923).

(20) V. Gutmann, *Monatsh.*, **82**, 473 (1951).

(21) M. H. Moissan, *Compt. rend.*, **100**, 272 (1885).

(22) W. Finkelstein, *Z. physik. Chem.*, **115**, 303 (1925). Somewhat contradictory results are reported by F. Krafft and R. Neumann, *Ber.*, **34**, 565 (1901), who do not, however, give complete data.

(23) (a) J. Meyer, *Z. anorg. Chem.*, **118**, 1 (1923); (b) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 976.

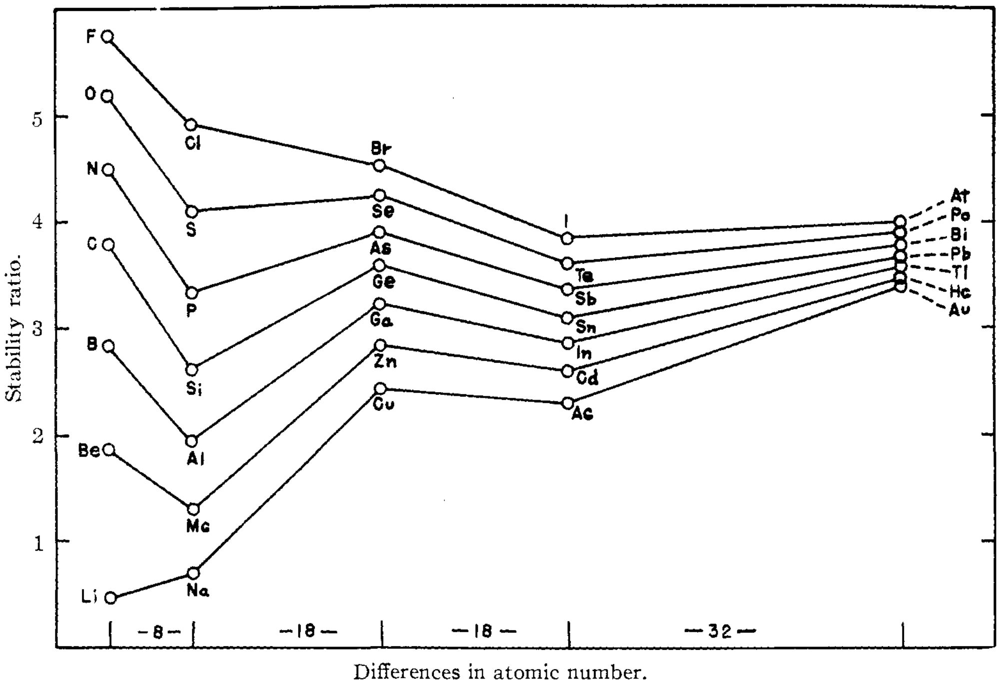

Fig. 1.—Group variations in electronegativity (*SR*).

A comparison of the data of Table I with the trends of Fig. 1 will disclose that in general the chemical "anomalies" are quite consistent with the variations in electronegativity. The use of these *SR* values as electronegativities to help explain such "anomalies" may be illustrated by a discussion of (1) the hydrolysis of silane compared to methane and germane, and (2) the non-existence of arsenic (V) chloride.

An important postulate[2] is that atoms change to equal electronegativity in a molecule, the final value being the geometric mean of the *SR*'s of all the individual atoms before combination.

The stability ratios of hydrogen (determined empirically) and of carbon, silicon and germanium are 3.55, 3.79, 2.62 and 3.59. From these values and the above postulate, germane is expected to contain practically completely non-polar bonds, while the bonds in methane are only very slightly polar, with hydrogen positive, and the bonds in silane are considerably more polar, with hydrogen negative. According to the theory, the electronic spheres of hydrogen and germanium have undergone no appreciable change in average density by forming the compound, germane. In the formation of methane, the sphere of the carbon atom has expanded very slightly, as the result of its assuming a partial negative charge. In the formation of silane, however, the spheres of the hydrogen atoms have expanded and the sphere of the silicon atom has contracted. The relative condition of hydrogen in each of these compounds is indicated by the *SR*'s of the molecules: CH_4, 3.59; SiH_4, 3.34; GeH_4, 3.55: hydrogen has changed in *SR* only by 0.04 in methane, and not at all in germane, but by −0.21 in silane.

From two viewpoints, ready hydrolysis of methane would not be expected. First, if the covalent coördination of a water molecule (or hydroxide ion) to the methane molecule is a prerequisite to hydrolysis, it is prohibited according to the Pauli principle. Second, there would be little tendency for the positive hydrogen of the water molecule to unite with the slightly positive hydrogen of the methane. The coördination of water or hydroxide ion to silane or germane, however, is not excluded; hence the ease of hydrolysis must depend on the condition of the hydrogen. In silane, it is negative and therefore can unite readily with the positive hydrogen of water to form molecular hydrogen.[24] In germane, however, the hydrogen is neutral and therefore has little tendency to combine with the hydrogen of water. The ease of hydrolysis of silane is probably increased by the greater energy of the silicon–oxygen bond, to be expected from the greater electronegativity difference between silicon and oxygen than between germanium and oxygen (ΔSR: O–Si, 2.59; O–Ge, 1.62; see item 7 of Table I).

Consider now the problem of the existence of phosphorus(V) chloride and antimony(V) chloride but not arsenic(V) chloride. Although the order of increasing non-polar covalent radius is P–As–Sb, the *SR*'s of these elements are 3.34, 3.91 and 3.37. That of chlorine is 4.93. The geometric mean *SR* for phosphorus(V) chloride is essentially the same as for antimony(V) chloride: 4.62, which means that the chlorine has only been able to expand enough to change in *SR* by 0.31, and still has far to go to reach the maximum stability represented by an *SR* of one. It has therefore lost relatively little of its oxidizing power, which helps explain why both compounds are good chlorinating agents.

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[24] Similarly, it is of interest that the *SR* of boron is 2.84, which is 20% less than that of hydrogen, compared with the 5% difference in Pauling's electronegativity values. *SR*'s thus indicate a more polar B–H bond, with more negative hydrogen, in better agreement with the chemical properties.

For arsenic(V) chloride, however, the *SR* would be 4.74, indicating that the chlorine would have expanded only enough to change in *SR* by 0.19. Here the bond would be even less ionic, and this compound would be expected not only to be an even more active chlorinating agent, but also it would be less stable. When it is considered that phosphorus(V) chloride is 13.5% dissociated in the vapor at 160°,[25] and wholly dissociated above 300°, and that antimony(V) chloride is likewise considerably dissociated even at its boiling point of 140°,[26] it is not surprising that arsenic(V) chloride has not been prepared.

There are, of course, other factors which complicate such chemical interpretations, especially for the compounds of the heavier atoms. One is the bond length, which together with the polarity of the bond has its effect on ionization. The ease of separation of a molecule into ions depends not only on the polarity of the bonds but also on the bond lengths; ionization may occur as easily for a less polar bond if the bond length is greater. This may help to explain the trend toward "increasing basicity" in a periodic group where the electronegativity actually alternates.

Another complicating factor is the apparent decrease in availability for bond formation, in certain elements, of the *s* electrons in the higher principal quantum levels. That is, the so-called "inert pair,"[27] (which may contribute to the instability of mercury compounds, causes the major valence of thallium to be one instead of three, causes lead to exhibit a valence of two in preference to four, and contributes largely to the instability of bismuth(V)) probably exerts an influence on the oxidizing properties of such elements as antimony and tellurium in their higher valence states, which would not be predicted on the basis of stability ratios alone.

Independent of such factors, the stability ratio theory seems both to be strengthened by its consistency with the many known chemical "anomalies" and to be useful in helping to explain them.

(25) W. Fischer and O. Jübermann, *Z. anorg. Chem.*, **235**, 337 (1938).

(26) Reference 23b, p. 794.

(27) (a) H. G. Grimm and A. Sommerfeld, *Z. Physik*, **36**, 36 (1926), (b) ref. 23b, pp. 287, 481, 617, 795, 798, 951.

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[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Vapor Pressures and Freezing Points of the System Nitrogen Tetroxide–Nitric Oxide

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The freezing points and vapor pressures of the system N_2O_4–NO have been determined in the composition range 0 to 16.85% by weight of NO, and in the temperature range 15 to −40°.

Introduction

The system nitrogen tetroxide–nitric oxide represents a rather unique combination of compounds. Nitrogen tetroxide in the liquid phase as well as in the gas phase dissociates reversibly into two molecules of nitrogen dioxide. Nitric oxide reacts either with nitrogen tetroxide or nitrogen dioxide to form nitrogen trioxide (N_2O_3) which also dissociates. The system, therefore, is complicated by at least two sets of equilibria which are not independent. Data on the freezing points and vapor pressures of mixtures of nitrogen tetroxide and nitric oxide are not only important parameters of the system, but can contribute to an understanding of the properties of N_2O_4–NO solutions. Wittorf,[1] and Baume and Robert[2] both investigated this system, but unfortunately the agreement between the results reported by these investigators is poor. The freezing points and vapor pressures, therefore, were redetermined in 1948 at the U. S. Naval Ordnance Test Station, Inyokern. The results of this investigation are in substantial agreement with those of Baume and Robert[2] over the range of compositions studied.

Purification of Nitrogen Tetroxide.—Nitrogen tetroxide about 99.5% pure as obtained from Mathieson Chemical Company was used as starting material. It was boiled in the presence of phosphorus pentoxide for about 16 hours, and then distilled into a container which was arranged so that dry oxygen could be bubbled through the dried nitrogen tetroxide to oxidize the last traces of nitric oxide. The purified material was then frozen and pumped on to remove as much oxygen as possible. All these operations were carried out in all glass apparatus containing no ground joints or stopcocks.

The purified material had a melting point of −11.23° (this is in good agreement with −11.20° obtained by Giauque and Kemp[3]) and froze to a colorless solid. The water content was about 0.024 ± 0.01% by weight according to the analytical work as carried out by the method of Whitnack and Holford.[4]

Preparation of Nitric Oxide.—The method given by Johnston and Giauque[5] for the preparation of nitric oxide appears to give a very pure material, but has the disadvantage of requiring a dependable supply of liquid nitrogen. It was therefore advisable to seek another method. Several methods of generation were tried, and the nitric oxide analyzed qualitatively to determine the impurities present. Nitrous oxide was detected by observing the transmission of a sample in the infrared region. Inert impurities were determined by oxidizing a sample in a eudiometer tube with an acid permanganate solution. The inert material was taken as the volume of gas remaining after all reaction had ceased. The method of preparation finally adopted consisted of adding a saturated solution of sodium nitrite to a saturated solution of ferrous sulfate in 35% sulfuric acid. This method was found to give no detectable amounts of N_2O, and a minimum amount of inert material, assumed to be nitrogen because it was not affected by solutions of permanganate, persulfate or thiosulfate, and did not support combustion.

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(1) N. V. Wittorf, *Z. anorg. Chem.*, **41**, 85 (1905).

(2) G. Baume and M. Robert, *Compt. rend.*, **169**, 968 (1919).

(3) W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

(4) G. C. Whitnack and C. J. Holford, *Anal. Chem.*, **21**, 801 (1949).

(5) H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929).