

Van Vechten J A. Quantum dielectric theory of electronegativity in covalent systems. I. Electronic dielectric constant. *Phys. Rev.* 182:891-905, 1969.
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Electronegativity difference is redefined as a scaling parameter generalizing the concept of valence difference. A procedure for its evaluation is developed in terms of the dielectric constant. The effects of d-electron states and of pressure are evaluated. The treatment is applied to 68 crystals. [The SCI® indicates that this paper has been cited in over 460 publications since 1969.]

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"This was the first in a three-part series^{1,2} that resulted from my thesis work under James C. Phillips. The object was to adapt the chemical concept of electronegativity to semiconducting crystals in order to delineate chemical trends in their electronic, optical, and thermochemical properties. It was a time of broad investigation of many semiconducting materials. Much data was waiting to be sorted into coherent patterns. There was also an eager audience for any means that would predict which compositions should be synthesized next. Thus, good timing is part of the reason it has been widely cited.

"Another part of the reason for so many citations may be that this paper, and the entire project that Phillips and I conducted, gained much initial notice because some regarded it as heresy. It seemed that the electronegativity theory of Linus Pauling, one of the most revered of all chemists, was being questioned by a young physics professor and his graduate student. In my view, this was a false perception; our contribution was evolutionary rather than revolutionary.

"The concept of electronegativity arose in the eighteenth century when the magnitude of the voltage appearing between different metals in an

acid solution was noted. It had been refined and given microscopic interpretation by J.J. Thomson (see reference 3, especially page 769) and by G.N. Lewis⁴ before Pauling made it a household concept with his Table of Elemental Electronegativities⁵ and his bond additivity approximation method of calculating heats of reaction for molecules. Pauling's elemental electronegativities could be calculated as (proportional to) the electrostatic potential due to the ion core at the boundary of the atom, one covalent radius from its center. (The ion core charge would be +3 for B, +4 for C, +5 for N, etc.) The Pauling scheme works very well for molecules but leads to several errors in predicting the heats of reaction in crystals. Phillips had proposed⁶ that these discrepancies could be resolved by taking account of the dielectric screening of this electrostatic interaction, which transfers charge from one atom to another. (Such screening is slight for molecules surrounded by vacuum.) This concept is now generally accepted and my paper is cited because it contains the 'nitty-gritty' details of the development and justification.

"Because dielectric screening varies with the environment (pressure, temperature, and distant elements), this approach led naturally beyond the bond additivity approximation and made possible subsequent estimates of phase diagrams, alloy miscibility, and other thermochemical parameters which cannot be treated in that approximation. It was also possible to 'predict' the crystal structure that various compositions would assume without discrepancies.

"Phillips and I worked a few years on extensions of this work. His book⁷ emphasizes the connection with the physics of band structures; my handbook chapter⁸ emphasizes thermochemistry.

"The initial notice of my thesis, evidenced in part by citations, benefited me in a way perhaps more dramatic than most. I was called to military service upon completion of it. Some thought I could best serve my country on an ammunition ship headed for Saigon. Tom C. Collins, then of Wright-Patterson Air Force Base, and others convinced them that I would be more useful in a technical capacity and I was ordered instead to the Naval Research Laboratory in Washington."

1. Van Vechten J A. Quantum dielectric theory of electronegativity in covalent systems. II. Ionization potentials and interband transition energies. *Phys. Rev.* 187:1007-20, 1969. (Cited 320 times.)
2. Quantum dielectric theory of electronegativity in covalent systems. III. Pressure-temperature phase diagrams, heats of mixing, and distribution coefficients. *Phys. Rev. B* 7:1479-507, 1973. (Cited 130 times.)
3. Thomson J J. The forces between atoms and chemical affinity. *Phil. Mag.* 27:757-89, 1914.
4. Lewis G N. The atom and the molecule. *J. Amer. Chem. Soc.* 38:762-85, 1916. (Cited 155 times since 1955.)
5. Pauling L. The nature of the chemical bond. IV. The energy of single bonds and the relative electronegativity of atoms. *J. Amer. Chem. Soc.* 54:3570-82, 1932. (Cited 145 times since 1955.)
6. Phillips J C. Dielectric definition of electronegativity. *Phys. Rev. Lett.* 20:550-3, 1968. (Cited 175 times.)
7. *Bonds and bands in semiconductors*. New York: Academic Press, 1973. 288 p. (Cited 435 times.)
8. Van Vechten J A. A simple man's view of the thermochemistry of semiconductors. (Keller S P. ed.) *Handbook on semiconductors. Volume 3. Materials, properties and preparation*. Amsterdam: North-Holland, 1980. p. 1-111.