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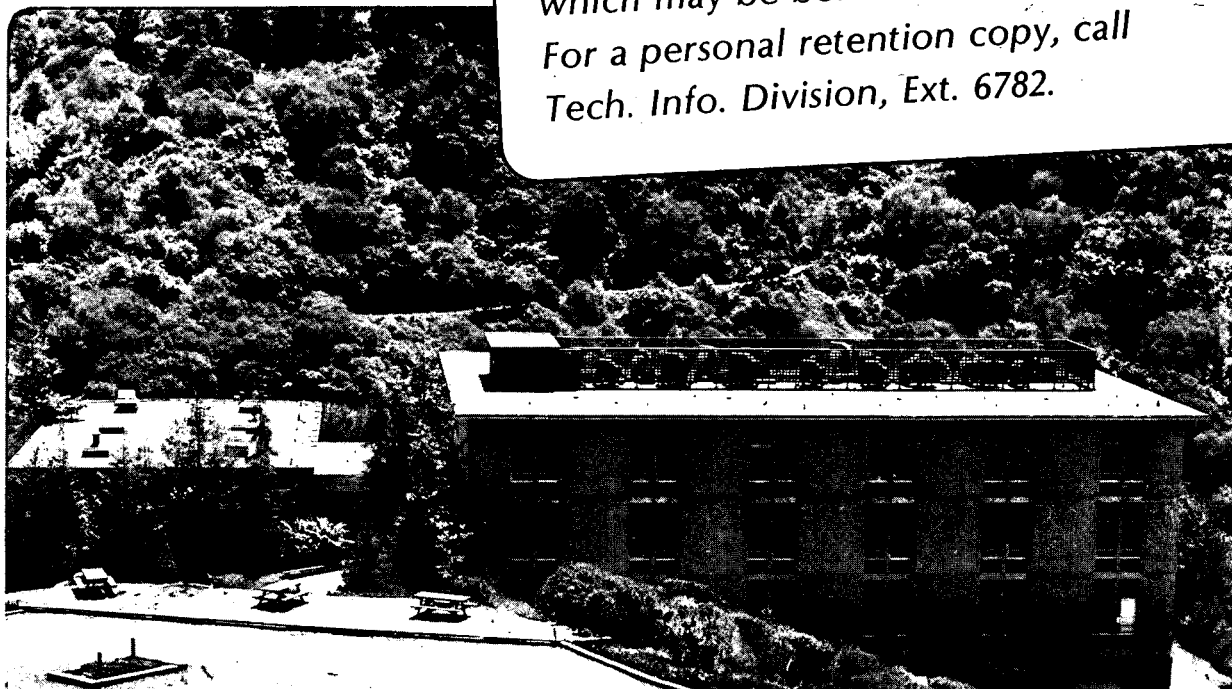
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IN SEMICONDUCTORS

M.E. Orazem and J. Newman

October 1983

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**Activity Coefficients of Electrons and Holes
in Semiconductors.**

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ABSTRACT

Dilute-solution transport equations with constant activity coefficients are commonly used to model semiconductors. These equations are consistent with a Boltzmann distribution and are invalid in regions where the species concentration is close to the respective site concentration. A more rigorous treatment of transport in a semiconductor requires activity coefficients which are functions of concentration. Expressions are presented for activity coefficients of electrons and holes in semiconductors. These activity coefficients are functions of concentration and are thermodynamically consistent. The use of activity coefficients in macroscopic transport relationships allows a description of electron transport in a manner consistent with the Fermi-Dirac distribution.

1. INTRODUCTION

The concentrations of holes and electrons in a semiconductor is given by the Fermi-Dirac distribution.^{1,2} A Boltzmann distribution is frequently used as an approximation to this distribution in statistical-mechanical analyses of semiconducting systems. Dilute-solution transport equations with constant activity coefficients, consistent with a Boltzmann distribution, are also used in characterizing the behavior of semiconducting systems. These approximate methods are popular because of their relative mathematical simplicity, but are invalid when electron or hole concentrations are close to the respective site concentrations in any region.

Calculation of individual ionic activity coefficients for electrons and holes has been proposed as a means of identifying the regions in which these approximations are justified. Rosenberg,³ Panish and Casey, Jr.,^{4,5} and Hwang and Brews⁶ have presented activity coefficients for electrons and holes that are functions of potential as well as concentration. Harvey⁷ discusses the separation of the activity coefficient into parts due to chemical and electrical effects. Landsberg and Guy⁸ present an activity coefficient based upon an Einstein relation that includes within it the nonidealities associated with the activity coefficient.⁹

Activity coefficients are derived here that are functions of concentration. This derivation is independent of the Einstein relation. These activity coefficients are thermodynamically consistent and can be used to check the validity of the Boltzmann function as an approximation to the Fermi-Dirac distribution. These coefficients can also be used in the application of macroscopic transport equations to semiconducting systems in a way that is generally valid.

2. THEORETICAL DEVELOPMENT

The electrochemical potential of a given species can arbitrarily be separated into terms representing a reference state, a chemical contribution, and an electrical contribution.¹⁰

$$\mu_i = \mu_i^\theta + RT \ln(c_i f_i) + z_i F \Phi, \quad (1)$$

where Φ is a potential which characterizes the electrical state of the phase and can be defined in a number of ways. The potential used here is the electrostatic potential which is obtained through integration of Poisson's equation.¹¹ Equation (1) can be viewed as the defining equation for the activity coefficient, f_i .

Under the assumption of a dilute solution, the flux of an individual species within the semiconductor is driven by a gradient of electrochemical potential;

$$N_i = c_i u_i \nabla \mu_i, \quad (2a)$$

or

$$f_i N_i = u_i RT \nabla(c_i f_i) - u_i F(c_i f_i) \nabla \Phi, \quad (2b)$$

where N_i is the flux of species i . Introduction of $A = c_i f_i e^{z_i F \Phi / RT}$ yields

$$f_i N_i = u_i RT e^{-z_i F \Phi / RT} \nabla A. \quad (3)$$

Under equilibrium conditions, $\nabla A = 0$, and

$$c_i f_i = A e^{-z_i F \Phi / RT} \quad (4)$$

where A is a constant. Under the assumption of a constant activity coefficient, equation (4) is consistent with a Boltzmann distribution.

The distribution of electrons in a semiconductor is characterized by the Fermi-Dirac function:

$$\frac{n_i}{g_i} = \left[1 + \exp[(E_i - E_f) / RT] \right]^{-1}, \quad (5)$$

where n_i is the number of electrons within an energy level E_i with degeneracy g_i . The Fermi energy E_f is a statistical parameter given the units of J/mol and defined as the energy at which the probability of occupancy of a state is one half. The Fermi-Dirac distribution enters into the transport development (equations 2, 3, and 4) through introduction of individual ionic activity coefficients: one for electrons and one for holes.

Through Fermi-Dirac statistics the concentration of conduction electrons is given by

$$n = \int_{E_c}^{\infty} \frac{N(E)}{1 + \exp[(E-E_f)/RT]} dE, \quad (6)$$

and the concentration of holes by

$$p = \int_{E_o}^{E_v} \left[1 - \frac{1}{1 + \exp[(E-E_f)/RT]} \right] N(E) dE. \quad (7)$$

If the distribution of available energy levels is narrow or RT is small, the valence and conduction electrons can be characterized by single-valued energy levels, E_v (the highest energy level of the valence band) and E_c (the lowest energy level of the conduction band), respectively. Thus;

$$n = \frac{1}{1 + \exp[(E_c-E_f)/RT]} \int_{E_c}^{\infty} N(E) dE, \quad (8)$$

or

$$n = \frac{N_c}{1 + \exp[(E_c-E_f)/RT]}, \quad (9)$$

where N_c is the concentration of conduction-energy sites for electrons. A similar term, N_v , is defined as the concentration of valence-band sites.

>From the definition of the electrochemical potential, the chemical activity,

$$a_i = c_i f_i, \quad (10)$$

can be expressed as

$$a_i = \exp \left[\frac{\mu_i - \mu_i^{\circ} - z_i F \Phi}{RT} \right]. \quad (11)$$

In equation (9), the concentration of conduction electrons is given as a function of the Fermi energy level. The energy E_c in this equation depends upon potential as

$$E_c = E_c^{\circ} + z_i F \Phi, \quad (12)$$

where E_c° is a constant, independent of potential. The electrochemical potential of conduction electrons and the Fermi Energy are related by an arbitrary constant;

$$\mu_{e^-} = E_f + \mu_{e^-}^{\circ}. \quad (13)$$

Equations (11) through (15) can be combined to yield

$$f_{e^-} = \frac{\exp[(\mu_{e^-}^* - \mu_{e^-}^{\theta} + E_c)/RT]}{N_c} \left[\frac{1}{1 - n/N_c} \right], \quad (14)$$

where f_{e^-} is dimensionless. The secondary reference state quantities, E_c^* , $\mu_{e^-}^*$, and $\mu_{e^-}^{\theta}$, are chosen to allow the activity coefficient to approach unity as the concentration of conduction electrons approaches zero. Thus, the activity coefficient is obtained as a function of composition;

$$f_{e^-} = \frac{1}{1 - n/N_c}, \quad (15)$$

The activity coefficient of conduction electrons is presented in Figure 1 as a function of dimensionless concentration n/N_c .

A similar activity coefficient can be obtained for the holes as

$$f_{h^+} = \frac{1}{1 - p/N_v}. \quad (16)$$

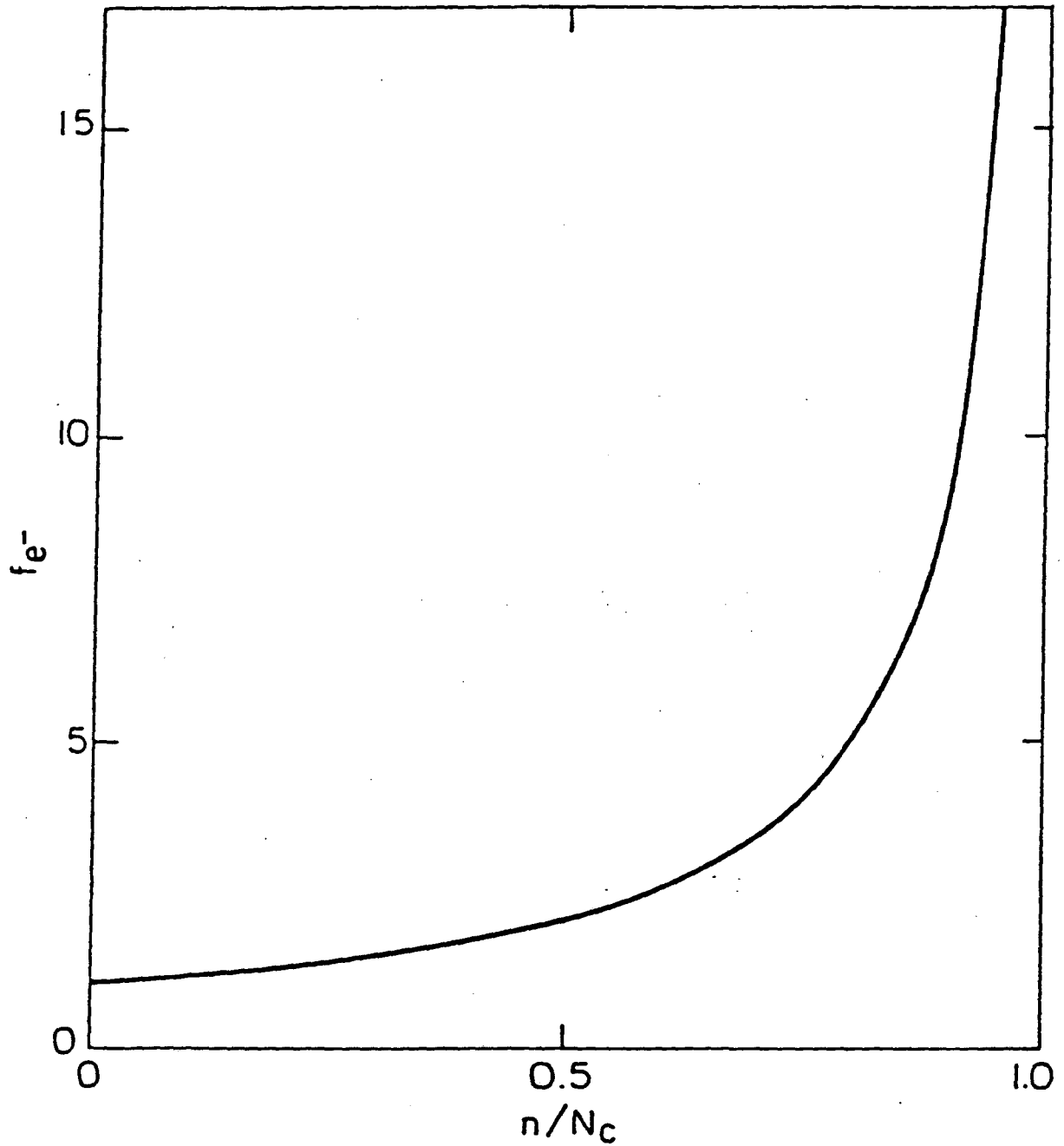
The assumption of unity activity coefficients is in harmony with the assumption of the Boltzmann limits to the Fermi-Dirac distribution. Use of the Fermi-Dirac distribution results in activity coefficients that are functions of concentration.

3. DISCUSSION

Equations (15) and (16) are consistent with the form of the activity coefficients

$$f_{e^-} = \frac{N_c}{n} e^{(E_f - E_c)/RT} e^{\Delta E/RT}$$

presented by Hwang and Brews⁶ and Landsberg and Guy.⁸ These authors include a term $e^{\Delta E/RT}$ for the shift in electron energy due to the occupation of energy levels above E_c at high electron concentrations.¹² Under the assumption that $\Delta E = 0$, equation (15) is recovered by introduction of the Fermi-Dirac distribution function for electrons. Calculation of ΔE requires knowledge of the electron site distribution $N(E)$.



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Figure 1. The activity coefficient of conduction electrons as a function of dimensionless concentration.

The activity coefficients defined above can be checked for consistency with the Fermi-Dirac function. Introduction of the activity coefficient presented for electrons in equation (15) into the respective Boltzmann distribution,

$$nf_{e^-} = N_c e^{(E_c - E_f)/RT}, \quad (17)$$

recovers the Fermi-Dirac distribution,

$$\frac{n}{N_c} = \frac{1}{1 + e^{-(E_c - E_f)/RT}}. \quad (18)$$

The same is true for the activity coefficient for holes.

A measure of internal thermodynamic consistency is obtained from the second cross-derivative of the Gibbs function, i.e.,

$$\left(\frac{\partial \mu_i}{\partial c_k} \right)_{T,P,c_j \neq k} = \left(\frac{\partial \mu_k}{\partial c_i} \right)_{T,P,c_j \neq i}, \quad (19)$$

where i and k represent components of the system that are not the solvent. This necessary condition for thermodynamic consistency is expressed for the system described here as

$$\frac{RT}{f_{e^-}} \left(\frac{\partial f_{e^-}}{\partial p} \right)_{T,P,n} = \frac{RT}{f_{h^+}} \left(\frac{\partial f_{h^+}}{\partial n} \right)_{T,P,p}. \quad (20)$$

This condition is satisfied. (Equation 19 is properly stated in terms of mole numbers rather than concentrations. For the dilute systems involved here, lattice expansion is ignored, and the two are equivalent.)

Use of macroscopic relations for thermodynamics and transport in regions of nonzero electric charge density raises some interesting philosophical questions because transport and thermodynamic properties are not easily measurable as functions of composition including arbitrary departures from electroneutrality. Fortunately, the semiconductors of interest are extremely dilute compared to even dilute aqueous solutions, and theoretical expressions such as the Fermi-Dirac distribution can be used with some confidence. Note that individual ionic activity coefficients are here being introduced in regions of net charge.

The extreme dilution of the semiconductors is also a justification for using the simple transport equation (2a) rather than the multicomponent diffusion equation,¹⁰ which includes interactions of solute species, and for using the approximate thermodynamic test embodied in equation (19).

4. CONCLUSIONS

Activity coefficients are derived here that are functions of concentration. These activity coefficients are thermodynamically consistent and can be used to check the validity of the Boltzmann function as an approximation to the Fermi-Dirac distribution. These coefficients can also be used in the application of macroscopic transport equations to semiconducting systems.

5. ACKNOWLEDGEMENT

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