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Correction: Nonequilibrium thermodynamic model of thermoelectricity and thermodiffusion in semiconductors

Semen N. Semenov  ^a and Martin E. Schimpf  ^b

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Correction for 'Nonequilibrium thermodynamic model of thermoelectricity and thermodiffusion in semiconductors' by Semen N. Semenov *et al.*, *Phys. Chem. Chem. Phys.*, 2023, 25, 6790–6796, <https://doi.org/10.1039/D2CP05065J>.

The authors would like to make changes to eqn (2), (3), (5), (28), (29) and Table 2 in the published manuscript. The corrections pertain to the term $\mp n_{e(h)} e_0 \nabla \Phi$ (where $n_{e(h)}$ is the numeric concentration of electrons (holes), e_0 is the elementary charge, and Φ is the electric potential), inserted into eqn (3) by analogy with the literature. However, a difference in the present work is that the effect described by this term is already taken into account in eqn (2) and (3) by the use of the electrochemical potential $\tilde{\mu}_{e(h)} = \mu_{e(h)} \mp e_0 \Phi$ [where $\mu_{e(h)}$ is the chemical potential of the electron (hole)]. There is no need for this term in the open-circuit systems, although its presence as the ohmic voltage in the closed circuits causes no objections.

Eqn (2) expresses the gradient of the electrochemical potential of the electron or hole:

$$\nabla \tilde{\mu}_{e(h)} = \frac{\partial \mu_{e(h)}}{\partial n_{e(h)}} \nabla n_{e(h)} + \frac{\partial \mu_{e(h)}}{\partial T} \nabla T \mp e_0 \nabla \Phi. \quad (2)$$

However, the electrochemical potential is the thermodynamic function of the temperature and concentration and can change in space only through the change of these physical parameters. The term $\mp e_0 \nabla \Phi$ should be written as $\mp e_0 \frac{\partial \Phi}{\partial n_{e(h)}} \nabla n_{e(h)} \mp e_0 \frac{\partial \Phi}{\partial T} \nabla T$. Since the considered thermoelectric potential demonstrates no concentration dependence, eqn (2) should be written correctly as

$$\nabla \tilde{\mu}_{e(h)} = \frac{\partial \mu_{e(h)}}{\partial n_{e(h)}} \nabla n_{e(h)} + \frac{\partial (\mu_{e(h)} \mp e_0 \Phi)}{\partial T} \nabla T. \quad (\text{corrected 2})$$

Substituting the corrected eqn (2) into the equation for the electron or hole flux

$$\begin{aligned} \vec{J}_{e(h)} = & -\frac{n_{e(h)} L_{e(h)}}{T} \left\{ n_{e(h)} \frac{\partial \mu_{e(h)}}{\partial n_{e(h)}} \nabla n_{e(h)} \mp n_{e(h)} e_0 \nabla \Phi + n_{e(h)} \right. \\ & \times \left[\frac{\partial (\mu_{e(h)} \mp e_0 \Phi)}{\partial T} + \frac{\mu_{e(h)} \mp e_0 \Phi + q_{e(h)}}{T} \nabla T \right] \Bigg\}, \end{aligned} \quad (3)$$

where $L_{e(h)}$ is the Onsager kinetic coefficient, we obtain for the open-circuit system

$$\left\{ n_{e(h)} \frac{\partial \mu_{e(h)}}{\partial n_{e(h)}} \nabla n_{e(h)} + n_{e(h)} \left[\frac{\partial (\mu_{e(h)} \mp e_0 \Phi)}{\partial T} + \frac{\mu_{e(h)} \mp e_0 \Phi + q_{e(h)}}{T} \nabla T \right] \right\} = 0 \quad (\text{corrected 3})$$

^a Institute of Biochemical Physics RAS, Kosygin Street 4, 119334, Moscow, Russia. E-mail: sem@triniti.ru

^b Department of Chemistry, Boise State University, Boise, ID, USA. E-mail: mschimpf@boisestate.edu



and

$$\vec{J}_{e(h)} = -\frac{n_{e(h)}L_{e(h)}}{T} \left\{ \begin{array}{l} n_{e(h)} \frac{\partial \mu_{e(h)}}{\partial n_{e(h)}} \nabla n_{e(h)} \mp n_{e(h)} e_0 \nabla \Phi_{\text{Ohm}} + \\ n_{e(h)} \left[\frac{\partial (\mu_{e(h)} \mp e_0 \Phi)}{\partial T} + \frac{\mu_{e(h)} \mp e_0 \Phi + q_{e(h)}}{T} \right] \nabla T \end{array} \right\}, \quad (\text{corrected } 3')$$

where Φ_{Ohm} is the electric voltage proportional to the density of electric current through the system with the opposite sign. It is the ohmic potential inserted in the equation for the flux of the charge carriers according to the Ohm law expressed as a constitutive equation. According to the foregoing reasonings, eqn (5) should be ignored for the open-circuit systems.

The calculations of the electron and hole chemical potentials yielding eqn (15) keep the validity:

$$\tilde{\mu}_{e(h)} = \frac{\mu_0 \pm A}{2} \pm \frac{3}{4} k_B T \ln \frac{m_h}{m_e} \mp e_0 \Phi, \quad (15)$$

where μ_0 is the chemical potential of the parent atom yielding in dissociation an electron and hole, A is the band gap, and m_e and m_h are the effective masses of the electron and hole, respectively. Incorporating eqn (15) and using the corrected eqn (3), we obtain the corrected eqn (28) and (29) for the Seebeck coefficient:

$$\frac{\partial \Phi}{\partial T} = \frac{1}{4e_0} \left(\frac{\partial A}{\partial T} + \frac{3}{2} k_B \ln \frac{m_h}{m_e} \right) \quad (28)$$

$$\frac{\partial \Phi}{\partial T} = \frac{1}{2e_0} \left(\frac{\partial A}{\partial T} + \frac{3}{2} k_B \ln \frac{m_h}{m_e} \right) \quad (\text{corrected } 28)$$

$$\frac{\partial \Phi}{\partial T} = \frac{1}{4e_0} \frac{\partial (\mu_e - \mu_h)}{\partial T} \quad (29)$$

$$\frac{\partial \Phi}{\partial T} = \frac{1}{2e_0} \frac{\partial (\mu_e - \mu_h)}{\partial T}. \quad (\text{corrected } 29)$$

The revised versions of the concluding expression for the Seebeck coefficient (eqn (28)) and the relevant columns of Table 2 are shown below. The values of the Seebeck coefficient have doubled after correction.

$$\frac{\partial \Phi}{\partial T} = \frac{1}{2e_0} \left(\frac{\partial A}{\partial T} + \frac{3}{2} k_B \ln \frac{m_h}{m_e} \right)$$

Material	Standard Seebeck coefficient $\frac{d\Phi}{dT}$, $\mu\text{V K}^{-1}$
Ge	27.20 ²⁰
InAs	58.82; ²⁰ 166.70–207.00 ²¹
InP	−3.04 ²⁰
GaAs	−29.52; ²⁰ 116.30–143.52 ²¹
Si	50.68 ²⁰
GaP	3.08 ²⁰
AgKTe	116.20 ²²

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

