

CALIBRATION COEFFICIENT OF A HEAT FLOW DSC

Part III. Electromotive force of a thermocouple as a function of temperature

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Thermodynamic model for the quantitative description of the electromotive force in a thermocouple has been developed. Thermodynamic equilibrium was applied to the system of electrons in two metals in a contact, contrary to the consideration of the dynamics of electrons in a metal under external temperature gradient in the previous classical (Drude) and quantum (Sommerfeld) approaches.

The new model has two parameters, the 'universal' sensitivity ε_0 and the characteristic temperature of a particular thermocouple Θ_V , and quite simple expression for the emf $\Delta U = \varepsilon_0(T - \Theta_V \ln(1 + T/\Theta_V))$ and sensitivity $\varepsilon(T) = \varepsilon_0 T / (\Theta_V + T)$. The model is shown to fit the experimental data very well at low temperatures. At high temperatures, the model is less accurate.

The characteristic temperature Θ_V depends on the difference between the electron heat capacity coefficients $\gamma_1 - \gamma_2$ of two metals in the thermocouple. The greater the difference, the higher the sensitivity of the thermocouple.

Keywords: DSC, emf, Seebeck effect, thermocouple, thermodynamics

Introduction

In the previous report on the theory of sensitivity calibration of DSC, it was shown that the calibration coefficient $k(T)$ of a sensor depends on two phenomena, (1) heat transfer between crucible and surroundings and (2) the electromotive force (emf) of a thermocouple which the sensor is made of. Analysis of the heat transfer has allowed us to reveal the functional relation between the calibration coefficient and temperature, with thermophysical parameters of a DSC cell as coefficients [1]:

$$k(T) = \frac{\varepsilon(T)}{S_1 \frac{\lambda}{l} + 4\varepsilon\sigma S_2 T^3} = \varepsilon(T) \frac{1}{A + BT^3} \quad (1)$$

where S_1 is the area of a contact between a crucible and sensor, S_2 is the area of the crucible exposed to the radiation, λ is the coefficient of heat conductivity, l is the distance between a heat source and a sample holder, ε is the emissivity of the substance which the crucible is made of, σ is the Stefan's constant, and $\varepsilon(T)$ is the sensitivity of a thermocouple, the derivative of the emf with respect to temperature. The relationship (1) was used for the development of the optimal calibration procedure [2]. The emf is usually borrowed from the tables or calculated after polynomials of a high order (up to 14).

Electromotive force of a thermocouple as a function of temperature was derived by Drude (1900)

from the theory of an electron gas in a metal. The theory predicted the constant value for the sensitivity of a thermocouple

$$\varepsilon = \frac{k_B}{2e} \quad (2)$$

which is evidently incorrect. Here, k_B is the Boltzmann constant and e is the elementary charge. Improvement of the Drude theory by using the Fermi–Dirac distribution function results in the equation

$$\varepsilon(T) = \frac{\pi^2}{6} \frac{k_B^2}{eE_f} T \quad (3)$$

where E_f is the Fermi energy. The equation has two disadvantages. First, it predicts that $\varepsilon(T)$ is a linear function of temperature. This is, in fact, not true. Second, the values of $\varepsilon(T)$ calculated after the equation turned out to be too small as compared with experimental data. These two models of the emf are described in detail in [3].

After the analysis of the evaluations yielding the linear regression between the sensitivity of a thermocouple and temperature in the quantum model, we concluded that this is the direct result of the Sommerfeld expansion (Appendix). The expansion yields the energy of electrons in a form of a polynomial with even exponents of temperature: T^2 , T^4 , T^6 , etc. As $\varepsilon(T)$ is the derivative of the emf with respect to temperature, it is the polynomial with odd ex-

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ponents: T, T^3, T^5 , etc. In the final Eq. (3), only the first term with T is used and the rest are omitted. Both models, of Drude and Sommerfeld, consider the dynamics of electrons, their movement under external temperature gradient. Thermodynamics was not involved in those considerations.

The objective of this work was to develop alternative, thermodynamic, way for the evaluation of the emf and to create a more adequate theory for the quantitative description of the electromotive force. This allows us to use a more realistic equation for the sensitivity of a thermocouple $\varepsilon(T)$. Together with the recent relationship between $\varepsilon(T)$ and $k(T)$, this forms the complete theoretical background for calorimetric measurements by using a heat-flow sensor made of a thermocouple.

The model

Quantum effects in the system of electrons in a metal

The distribution of electrons over the energy levels in a metal obeys the Fermi–Dirac statistics:

$$f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \tag{4}$$

where E is the energy of an electron, μ is the chemical potential, k_B is the Boltzmann constant and T is the temperature. The chemical potential of the electrons in a metal is equal to the Fermi energy (E_f). The value of E_f is different for different metals, and is typically greater than 10^4 K (81600 K for Cu, 63800 K for Ag, 64200 K for Au, 130000 K for Fe, 110000 K for Zn, 136000 K for Al, etc.). To calculate the parameters of electrons in a metal, one should use the distribution function (4) together with the function of density of states $\rho(E)$, which describes how many energy levels of electrons there are in the interval of energy

$$dN(E) = \rho(E)dE \tag{5}$$

The number of electrons in the same energy interval is

$$dN(E) = \rho(E)f(E)dE \tag{6}$$

Any parameter of the electronic system is calculated using product $\rho(E)f(E)$. For example, average energy is

$$\langle E \rangle = \int_0^\infty E\rho(E)f(E)dE \tag{7}$$

Rigorous analytical integration for such an expression is impossible. To proceed the evaluation, Sommerfeld expansion is used. In application to the emf as a function of temperature, it yields a polynomial

$$\Delta U(T) = \sum_{i=0}^\infty c_i T^{2i} \tag{8}$$

and

$$\varepsilon(T) = \frac{d\Delta U}{dT} = \sum_{i=1}^\infty 2ic_i T^{2i-1} \approx 2c_1 T \tag{9}$$

The evaluation is described in more detail in the Appendix.

Our approach to the evaluations with the Fermi–Dirac distribution

Distribution function (4) is not only the function of energy, but also of temperature. To indicate it clearly, we will denote it by $f(E, T)$. At extremely low temperatures ($T \rightarrow 0$), the exponent in the denominator of the distribution function $f(E, T)$ changes drastically only in the nearest vicinity of E_f , with the large negative value for $E - E_f < 0$ and large positive for $E - E_f > 0$. In this case, electron states with $E < E_f$ are completely occupied and those with $E > E_f$ are completely vacant. The distribution function becomes a step function:

$$f(E, 0) = \begin{cases} 1; & E - E_f < 0 \\ 0; & E - E_f > 0 \end{cases} \tag{10}$$

Figure 1 shows this distribution function. The step diffuses when temperature increases, and partly occupied states appear in the vicinity of E_f . The less the temperature, the narrower the vicinity. If we investigate the changes in parameter F of the electronic system with temperature, we can consider the difference

$$\begin{aligned} \langle F_T \rangle - \langle F_0 \rangle &= \int_0^\infty F(E)\rho(E)f(E, T)dE - \\ &- \int_0^\infty F(E)\rho(E)f(E, 0)dE = \\ &= \int_0^\infty F(E)\rho(E)[f(E, T) - f(E, 0)]dE \end{aligned} \tag{11}$$

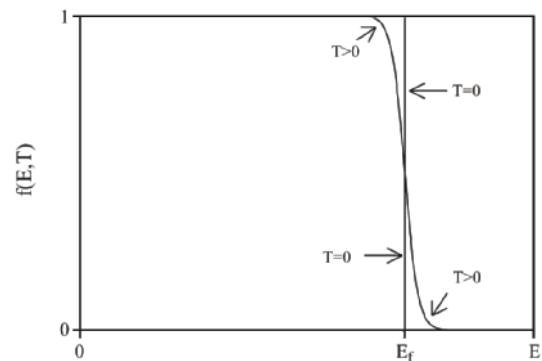


Fig. 1 Fermi–Dirac distribution function at a finite and zero temperature

Parameter F is considered to be a function of E . Otherwise, it is a constant and factored out from the integrand:

$$\begin{aligned} \langle F \rangle &= \int_0^{\infty} F\rho(E)f(E,T)dE = \\ &= F \int_0^{\infty} \rho(E)f(E,T)dE = F \cdot \text{const} \end{aligned} \quad (12)$$

The integrand in Eq. (11) differs from zero only in the vicinity of E_f , where $f(E,T)$ and $f(E,0)$ differ significantly from one another. The greatest difference (of 0.5) is at $E=E_f$. It decreases twenty times for $E-E_f=3k_B T$. Even for room temperature (300 K), such a difference is only 1/50 of E_f for most metals. Model function of $\rho(E)$ is usually considered to be proportional to the square root of energy, and $\rho(E_f+3k_B T)$ differs from $\rho(E_f-3k_B T)$ by 2%. Thus, $\rho(E)$ can be considered constant and factored out from the integrand.

We can apply this to the calculation of the number of electrons (N_T^+) with $E>E_f$. Only those electrons are involved in the electric processes in a metal. According to Eq. (11)

$$N_T^+ = N_0^+ + \int_{E_f}^{\infty} \rho(E)[f(E,T)-f(E,0)]dE \quad (13)$$

where $N_0^+=f(E,0)=0$, for all energy levels with $E>E_f$ are vacant at $T=0$ according to Eq. (10). Again, $\rho(E)$ is factored out from the integrand as $\rho(E_f)$. Denoting the difference $E-E_f=E^+$, we calculate the number of electrons with energy exceeding the Fermi energy:

$$\begin{aligned} N_T^+ &= \rho(E_f) \int_0^{\infty} \frac{dE^+}{e^{\frac{E^+}{k_B T}} + 1} = \\ &= \rho(E_f) k_B T \int_0^{\infty} \frac{1}{e^{\frac{E^+}{k_B T}} + 1} d\left(\frac{E^+}{k_B T}\right) \end{aligned} \quad (14)$$

The integrand becomes simpler after the substitution $t = e^{E^+/k_B T}$; $dt=td(E^+/k_B T)$:

$$\begin{aligned} N_T^+ &= \rho(E_f) k_B T \int_1^{\infty} \frac{dt}{t(t+1)} = \\ &= \rho(E_f) k_B T \int_1^{\infty} \frac{dt}{t} - \frac{dt}{t+1} = \\ &= \rho(E_f) k_B T \ln \left(\frac{1}{1+t^{-1}} \right) \Big|_1^{\infty} = \rho(E_f) k_B T \ln 2 \end{aligned} \quad (15)$$

Thus, the number of the electrons involved in the electric processes, including the electromotive force, is proportional to temperature.

Constructing the Gibbs function

At the contact between two metals, the electrons flow readily through the boundary between them. If the metals differ in the Fermi energy (the chemical potential of electrons), the electrons of the metal with higher potential have to move to the metal with lower potential, decreasing the difference and changing simultaneously the total electric charge of each metal in the pair. One metal is charged with positive electricity and the other with equivalent negative. Electrostatic energy contributes to the total energy of electron system of a metal. Chemical potential of electrons is the total Gibbs energy of electron system divided by the number of electrons. Conventional difference in Gibbs energy with electrostatic contribution between two metals is

$$\Delta G = \Delta H - T\Delta S + \Delta U \Delta q \quad (16)$$

where ΔH is the difference in enthalpy, ΔS is the difference in entropy, ΔU is the electrostatic voltage between two metals, and Δq is the difference in electric charge that produces the voltage. By definition, enthalpy is

$$H = \int C_e dT \quad (17)$$

where C_e is the heat capacity of the electron system in a metal. At low temperatures, the heat capacity of electrons in a metal is proportional to temperature:

$$C_e = \gamma T \quad (18)$$

Enthalpy of the electron system in metal '1' is

$$H_1 = 1/2 \gamma_1 T^2 \quad (19)$$

The difference in enthalpy between two metals is

$$\Delta H = 1/2 (\gamma_1 - \gamma_2) T^2 \quad (20)$$

Entropy of a system is derived from the total number of the states w according to

$$S = k_B \ln w \quad (21)$$

The number of the states in the system of N electrons is equal to the number of permutations

$$w = N! \quad (22)$$

Applying Stirling's formula, we have the entropy of the system of N electrons:

$$S = k_B (N \ln N - N + 1/2 \ln(2\pi N)) \quad (23)$$

Part of electrons passes from one metal into the other at temperature T . The number of electrons passed (ΔN) is evidently a fraction of those with the energy exceeding the Fermi energy:

$$\Delta N = \alpha T \quad (24)$$

After that, the number of electrons in one metal increases by αT and decreases in the other one by the same number. Instead of N in formula (23) one should

use $N+\alpha T$ for one metal and $N-\alpha T$ for the other. Now, the difference in entropy between two metals is

$$\begin{aligned} \Delta S = & k_B[(N+\alpha T)\ln(N+\alpha T) - (N+\alpha T) + 1/2\ln(2\pi) + \\ & + 1/2\ln(N+\alpha T)] - k_B[(N-\alpha T)\ln(N-\alpha T) - \\ & - (N-\alpha T) + 1/2\ln(2\pi) + 1/2\ln(N-\alpha T)] = \\ = & k_B \left(N \ln \frac{N+\alpha T}{N-\alpha T} + \alpha T \ln(N^2 - \alpha^2 T^2) \right) - \\ & - k_B \left(2\alpha T - 1/2 \ln \frac{N+\alpha T}{N-\alpha T} \right) \end{aligned} \quad (25)$$

The increase in the number of electrons in one metal by αT and equal decrease in the other metal result in the difference in electric charge

$$\Delta q = 2e\alpha T \quad (26)$$

where e is the charge of an electron.

Evaluating the emf

In equilibrium, the difference in the Gibbs energy between two metals is equal to zero:

$$\Delta G = \Delta H - T\Delta S + \Delta U\Delta q = 0 \quad (27)$$

This allows us to deduce the formula for the electrostatic voltage between two metals:

$$\begin{aligned} \Delta U = & \frac{\gamma_1 - \gamma_2}{4e\alpha} T - \\ & - \frac{k_B}{2e\alpha} \left[N \ln \frac{N+\alpha T}{N-\alpha T} + \alpha T \ln(N^2 - \alpha^2 T^2) \right] - \\ & - \frac{k_B}{2e\alpha} \left(2\alpha T - 1/2 \ln \frac{N+\alpha T}{N-\alpha T} \right) \end{aligned} \quad (28)$$

The formula is too complicated for the analysis. We can simplify it for the case of low temperatures and small changes in the electric charge. For

$$\alpha T \ll N \quad (29)$$

one can use approximation

$$\ln(N \pm \alpha T) \approx N \ln(N \pm \alpha T) \quad (30)$$

instead of complete Stirling's formula. Now the expression for entropy becomes more simple

$$\begin{aligned} \Delta S = & k_B N \ln(N + \alpha T) - k_B N \ln(N - \alpha T) = \\ = & k_B N \ln \frac{N + \alpha T}{N - \alpha T} \approx k_B N \ln \left(1 + \frac{2\alpha T}{N} \right) \end{aligned} \quad (31)$$

The formula for the emf:

$$\Delta U = \frac{\gamma_1 - \gamma_2}{4e\alpha} T - \frac{k_B}{2e\alpha} N \ln \left(1 + \frac{2\alpha T}{N} \right) \quad (32)$$

Let us introduce a new parameter

$$\Theta_v = \frac{N}{2\alpha} \quad (33)$$

in the units of temperature. Formula (32) is arranged now

$$\Delta U = \frac{\gamma_1 - \gamma_2}{4e\alpha} T - \frac{k_B}{e} \Theta_v \ln \left(1 + \frac{T}{\Theta_v} \right) \quad (34)$$

There is a relationship between the factors of two terms on the right-hand side of the equation. This can be derived from the sensitivity of a thermocouple as follows:

$$\frac{d\Delta U}{dT} = \varepsilon(T) = \frac{\gamma_1 - \gamma_2}{4e\alpha} - \frac{k_B}{e} \frac{\Theta_v}{\Theta_v + T} \quad (35)$$

At zero temperature ($T=0$), there are no electrons with the energy greater than the Fermi energy in metals, no electrons to pass from one metal into the other. Both emf and the sensitivity are equal to zero. Considering $\varepsilon(0)=0$ in Eq. (35), we have

$$\frac{\gamma_1 - \gamma_2}{4e\alpha} = \frac{k_B}{e} = \varepsilon_0 \quad (36)$$

The final equation for the emf of a thermocouple is

$$\Delta U(T) = \varepsilon_0 \left[T - \Theta_v \ln \left(1 + \frac{T}{\Theta_v} \right) \right] \quad (37)$$

This is for a thermocouple with a working junction at temperature T and reference junction at zero temperature (0 K). The sensitivity of the thermocouple is the nonlinear function of temperature:

$$\varepsilon(T) = \varepsilon_0 \frac{T}{\Theta_v + T} \quad (38)$$

Equation (38) is to be used in Eq. (1) for the calibration coefficient of a DSC.

Analysis of the functional relations

Only two parameters are there in Eqs (37) and (38), ε_0 and Θ_v . The first parameter is the ratio of two fundamental constants, Boltzmann constant and elementary charge. Such a value can be considered a special constant with the particular physical meaning. It can be seen from Eq. (38) that the sensitivity of a thermocouple is always less than ε_0 , but approaches asymptotically that value in the limit of infinitely high temperature ($T \rightarrow \infty$):

$$\varepsilon_0 = \frac{k_B}{e} = 86.17 \mu\text{V K}^{-1} \quad (39)$$

One can consider ε_0 the highest limit for the sensitivity of thermocouples. At least, we do not know thermocouples with the sensitivity $\varepsilon(T)$ exceeding the value of $86.17 \mu\text{V K}^{-1}$. Thus, the first parameter of the model characterizes the electromotive force phenomena in general, not a particular thermocouple.

The second parameter of the model, Θ_V , characterizes the pair of the metals in a thermocouple. It is evident from the way how it was introduced in Eq. (33). This is the result of the division of the number of electrons in the metal by coefficient 2α . In turn, from Eq. (36)

$$2\alpha = \frac{\gamma_1 - \gamma_2}{2k_B} \quad (40)$$

A rough estimate of Θ_V can be derived from the combination of Eqs (33) and (40):

$$\Theta_V = \frac{2k_B N}{\gamma_1 - \gamma_2} \quad (41)$$

Considering the number of free electrons in a metal close to the number of atoms, we can use the Avogadro number N_0 . The formula for the estimation becomes

$$\Theta_V = \frac{2R}{\gamma_1 - \gamma_2} \quad (42)$$

where $R=k_B N_0$ is the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The electronic heat capacity coefficient γ is different for different metals, but usually less than $10 \text{ mJ mol}^{-1} \text{ K}^{-2}$. For example, $\gamma=3.4, 9.4, 2.4, 3.3$ and $6.55 \text{ mJ mol}^{-1} \text{ K}^{-2}$ for Rh, Pd, Os, Ir and Pt, respectively [4]. For other pure metals, the values are similar [5]. For alloys, the electronic heat capacity coefficient depends nonlinearly on the ratio of components, with a sharp increase in the narrow limits of composition. For $\text{UPt}_{5-x}\text{Au}_x$, γ increases from $100 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $x=0$ up to $700 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $x=1$ and then decreases again down to $100 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $x=2$ [6]. The value of $700 \text{ mJ mol}^{-1} \text{ K}^{-2}$ seems extremely large compared with the values for pure metals, but the comparison is not quite correct. Mole of a pure metal contains N_0 atoms, but the mole of $\text{UPt}_{5-x}\text{Au}_x$ contains $6N_0$ (six atoms per 'molecule'). Corrected for the number of atoms, the values of γ are 16, 116, and $16 \text{ mJ mol}^{-1} \text{ K}^{-2}$ for $x=0, 1$ and 2 , respectively. For $\text{Lu}(\text{Co}_{1-x}\text{Si}_x)_2$, γ increases from $24 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $x=0$ up to $39 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $x=0.1$ and then decreases again [7]. Here, one should divide the γ values by 3 atoms per molecule. Electronic heat capacity of alloys is greater than those of pure metals, and the alloys are among the most popular materials for thermocouples: constantan (60% Cu+40% Ni for type J and 55% Cu+45% Ni for type T), chromel (90% Ni+10% Cr), alumel (95% Ni+2.5% Mn+2% Al+0.5% Co), nicrosil (84.4% Ni+14.2% Cr+1.4% Si),

nisil (95.5% Ni+4.4% Si+0.1% Mg). Taking $\gamma_1-\gamma_2=0.1 \text{ J mol}^{-1} \text{ K}^{-2}$ in Eq. (42), as it is for $\text{UPt}_{5-x}\text{Au}_x$, we obtain $\Theta_V=166 \text{ K}$. Here we do not specify the second metal of the thermocouple, because it may be any pure metal with $\gamma<10 \text{ mJ mol}^{-1} \text{ K}^{-2}$. $\Theta_V=166 \text{ K}$ is the lowest estimate. For Pt–Rh thermocouple with $\gamma_{\text{Pt}}-\gamma_{\text{Rh}}=3.15 \text{ mJ mol}^{-1} \text{ K}^{-2}$, the estimate for Θ_V is 5300 K .

Characteristic temperature Θ_V defines the temperature range in which the thermocouple works. If Θ_V is small, the sensitivity increases rapidly with temperature, becoming close to the limiting value of ε_0 right near room temperature, and the thermocouple can be used at low temperatures. If Θ_V is large, the sensitivity increases slowly and it is better to use the thermocouple only at high temperatures.

Testing the equations for $\Delta U(T)$ and $\varepsilon(T)$

The emf was carefully investigated quantitatively many years ago for many types of thermocouples widely used in practice today. For example, the emf of thermocouple Pt:(Pt–Rh) was investigated as a function of temperature and Pt/Rh ratio about 100 years ago [8]. From time to time the emf of thermocouples is updated according to the current version of temperature scale (now ITS-90). There are two ways for the representation of the emf: tables and polynomials. To test the results of this work, we chose the tables and polynomials of NIST (the National Institute of Standards and Technology, USA) by two reasons. First, the NIST pays much attention to the calibration of DSCs [9]. Second, the polynomials are available for free in the www (<http://srdata.nist.gov/its90/main/>), together with the tables.

There are two points that we should take into consideration prior to the tests. First, all NIST polynomials are used with degrees Celsius ($t, ^\circ\text{C}$), but the thermodynamic model was developed for kelvins (T, K). Second, the reference junction of a thermocouple for the NIST polynomials is to be at 273.15 K (0°C), but at 0 K (-273.15°C) for the thermodynamic model. This produces a constant difference between the emf values evaluated after the polynomials and Eq. (37). To adapt the thermodynamic model to the form similar to the NIST polynomials, one should 'place' the reference junction at 273.15 K . It means that the voltage from $T=273.15 \text{ K}$ (constant value) must be subtracted from the voltage at temperature T :

$$\begin{aligned}
\Delta U(T) - \Delta U(273.15) &= \varepsilon_0 \left[T - \Theta_V \ln \left(1 + \frac{T}{\Theta_V} \right) \right] - \\
&- \varepsilon_0 \left[273.15 - \Theta_V \ln \left(1 + \frac{273.15}{\Theta_V} \right) \right] = \\
&= \varepsilon_0 [(T - 273.15)] - \\
&- \varepsilon_0 \left[\Theta_V \ln \frac{\Theta_V + 273.15 + (T - 273.15)}{\Theta_V + 273.15} \right] = \\
&= \varepsilon_0 \left[t - \Theta_V \ln \left(1 + \frac{t}{\Theta_V + 273.15} \right) \right] = \Delta U(t)
\end{aligned} \quad (43)$$

One can use $\Delta U(t)$ here, because $t=T-273.15$. Equation (43) can be compared directly with the NIST polynomials for the emf. As for the sensitivity of a thermocouple, it is not necessary to adapt Eq. (38), because $\varepsilon(T)$ is the derivative of ΔU with respect to temperature, and the addition or subtraction of a constant vanishes after differentiation. To compare $\varepsilon(T)$ calculated after Eq. (38) and NIST polynomials with one another, suffice it to plot them against the single temperature scale.

Thermodynamic theory of the emf was developed under the assumption that the temperature is very low as compared with Θ_V . For the test, we should choose a thermocouple with the data available for low temperatures but with the greatest value of Θ_V . Equation (43) allows us to estimate Θ_V for the thermocouple working at low temperatures. Thermocouples used in the testing are listed in Table 1. Four thermocouples (types E, K, N, T) are tabulated starting from -270°C . Polynomials for the temperature range of -270 – 0°C are available for each of them. We used Eq. (43) for the calculation of Θ_V , with $\Delta U(t=-270)$ taken from the tables. The results are in Table 1. For thermocouples J, R and S, the temperature intervals were of -210 – $(+90)$, -50 – $(+250)$ and -50 – $(+250)^\circ\text{C}$, respectively. The greatest value of Θ_V is for thermocouple S (4180 K) and the least for E (159 K). For the test, we need a thermocouple with the least value of T_{\min}/Θ_V , where T_{\min} is the low-temperature limit of a polynomial or/and table. The values of T_{\min}/Θ_V are also listed in Table 1. Thermocouple N with of $T_{\min}/\Theta_V=0.006$ is the best choice.

Experimental (NIST polynomial) and theoretical (Eq. (43)) functions $\Delta U(t)$ are shown in Fig. 2a. Two functions agree well with one another. Two lines on the figure are too close, overlapping with one another, and the difference $\Delta U_{\text{pot}} - \Delta U_{\text{theor}}$ is plotted especially to show it on an enlarged scale. The values of $\Delta U(t)$ increase from -270 to 0°C by about 4.5 mV, but the difference between experimental and theoretical functions is less than 0.05 mV. Theoretical and experimental functions $\varepsilon(T)$ are shown in Fig. 2b. One may conclude that

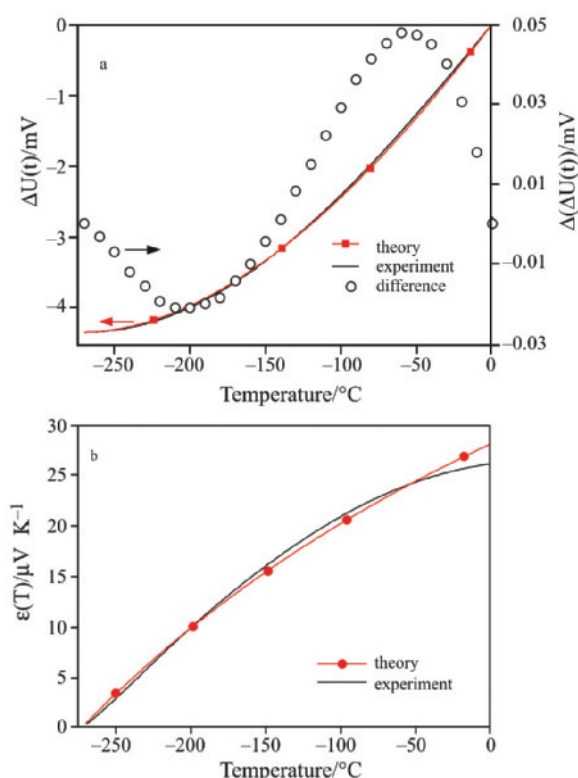


Fig. 2 Comparison between theoretical and experimental values of the a – emf and b – sensitivity for thermocouple type N. The difference between the theory and experiment is shown vs. the right Y-axis

the theory with only one parameter (Θ_V) fits experimental values of a real thermocouple surprisingly well.

The agreement between theory and experimental data for all NIST thermocouples is evident from Fig. 3a. Here, the values of the sensitivity are shown in transformed coordinates. Equation (38) can be rewritten in the form

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0} + \frac{\Theta_V}{\varepsilon_0} \frac{1}{T} \quad (44)$$

This is the equation of a straight line

$$y = a + bx \quad (45)$$

with $x=1/T$ and $y=1/\varepsilon$. ‘Low-temperature’ thermocouples (E, K, N and T) fit a straight line well, but R and S do not. These thermocouples are made of Pt:(Pt–Rh) pairs with minor changes in composition: 13% of Rh for R and 10% for S. One more thermocouple, type B (30% Pt–70% Rh)–(6% Pt–94% Rh), was not used in the test. It has an anomaly in the emf near room temperature, with the sensitivity changing in sign from negative to positive: $\varepsilon < 0$ for $t < 20^\circ\text{C}$ and $\varepsilon > 0$ for $t > 20^\circ\text{C}$. It evidently conflicts with the theory that predicts a constant sign and steady growth of $\varepsilon(T)$.

High-temperature part of Fig. 3a is shown in Fig. 3b. For all thermocouples except T the linearity

Table 1 Data on the thermocouples used in the testing of the theory, parameters of the NIST polynomials, and calculated values of Θ_V

Type	Metal (alloy) 1 Metal (alloy) 2	T_{range} of a polynomial/ $^{\circ}\text{C}$	Polynomial order, n	$\Delta U(-270)/\text{mV}$	Θ_V/K	T_{range} of calculation/ $^{\circ}\text{C}$	T_{min}/Θ_V																																																										
E	chromel constantan	-270-0	13	-9.835	159		0.020																																																										
		0-1000	10					J	Fe constantan	-210-760	8		197	-210-90	0.32	760-1200	5	K	chromel alumel	-270-0	10	-6.458	325		0.010	0-1372	9	N	microsil nihil	-270-0	8	-4.345	564		0.006	0-1300	10	R	13% Rh/Pt Pt	-50-1064.18	9		4097	-50-250	0.054	1064.18-1664.5	5	1664.5-1768.1	4	S	10% Rh/Pt Pt	-50-1064.18	8		4180	-50-250	0.053	1064.18-1664.5	4	1664.5-1768.1	4	T	Cu constantan	-270-0	14
J	Fe constantan	-210-760	8		197	-210-90	0.32																																																										
		760-1200	5					K	chromel alumel	-270-0	10	-6.458	325		0.010	0-1372	9	N	microsil nihil	-270-0	8	-4.345	564		0.006	0-1300	10	R	13% Rh/Pt Pt	-50-1064.18	9		4097	-50-250	0.054	1064.18-1664.5	5			1664.5-1768.1	4					S	10% Rh/Pt Pt	-50-1064.18	8				4180					-50-250	0.053	1064.18-1664.5	4	1664.5-1768.1	4	T	Cu constantan
K	chromel alumel	-270-0	10	-6.458	325		0.010																																																										
		0-1372	9					N	microsil nihil	-270-0	8	-4.345	564		0.006	0-1300	10	R	13% Rh/Pt Pt	-50-1064.18	9		4097	-50-250	0.054	1064.18-1664.5	5			1664.5-1768.1	4					S	10% Rh/Pt Pt	-50-1064.18	8		4180	-50-250	0.053	1064.18-1664.5	4			1664.5-1768.1	4	T	Cu constantan			-270-0	14	-6.258	340				0.009	0-400	8		
N	microsil nihil	-270-0	8	-4.345	564		0.006																																																										
		0-1300	10					R	13% Rh/Pt Pt	-50-1064.18	9		4097	-50-250	0.054	1064.18-1664.5	5			1664.5-1768.1	4					S	10% Rh/Pt Pt	-50-1064.18	8		4180	-50-250	0.053	1064.18-1664.5	4			1664.5-1768.1	4					T	Cu constantan	-270-0	14	-6.258	340		0.009	0-400	8												
R	13% Rh/Pt Pt	-50-1064.18	9		4097	-50-250	0.054																																																										
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		1064.18-1664.5	4																																																														
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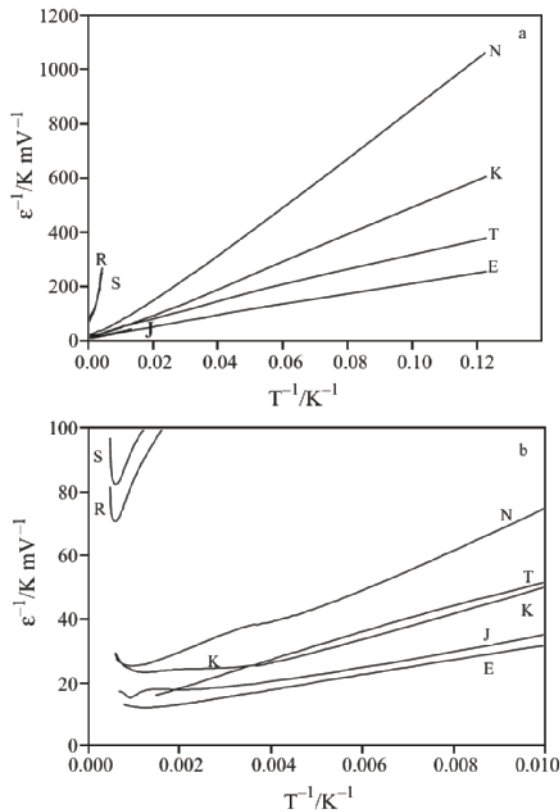


Fig. 3 Reciprocal sensitivity of thermocouples vs. reciprocal temperature. Types of the thermocouples are indicated by the letters. a – whole temperature interval and b – its high-temperature part are shown separately to demonstrate the deviation of the experimental data from the theoretical relationship at high temperatures

does not hold. Moreover, for all thermocouples (except T again) the $\varepsilon(T)$ function is not monotonous, increasing and then decreasing. The temperature of the maximum differ for different thermocouples. For example, the maximum is at 525°C for thermocouple type E, 800°C for J, and 1350°C for R.

We cannot explain the reason why the linearity is violated and why there is the change in sign of the sensitivity for thermocouple B. Probably, this is the result of complex topology of the Fermi surface. It is well known that the density of states $\rho(E)$ near the Fermi energy for metals is not described by a sphere with $S \sim E^{1/2}$, in fact, but by quite complicated surface that has been the subject of much investigation for many metals. For low-temperature emf, it does not matter what the surface is exactly, for it participates in the calculations as a factor (Eq. (14)). But at high temperatures it starts to affect the concentration of free electrons N_T^+ .

Conclusions

The thermodynamic model for the electromotive force in a thermocouple has been developed on the basis of the Gibbs energy. Contrary to the dynamic models of the emf, the new model predicts that the sensitivity of a thermocouple changes non-linearly with temperature. The model contains only two parameters. The first one (ε_0) is the universal constant characterizing the limiting value of the thermocouple sensitivity. The second one (Θ_V) is a characteristics of a particular thermocouple. Thermocouples with a high sensitivity at low temperatures have small Θ_V values. In turn, Θ_V depends on the difference in the electronic heat capacity coefficients ($\gamma_1 - \gamma_2$) of two metals in the thermocouple.

The thermodynamic model agrees well with the experimental data for low temperatures. Together with the recent theory of the relationship between the calibration coefficient of a DSC and the sensitivity of the thermocouple which the sensor is made of, the model reported in this work forms the complete theory of calorimetric measurements by using thermocouple sensors.

Appendix

Dynamic models for the evaluation of the electromotive force

The Drude theory considers the electrons in a metal as an ideal gas. The energy of gas particles (electrons) depends on the temperature according to conventional relationship

$$E = 3/2nk_B T = n \frac{mv^2}{2} \quad (\text{A1})$$

where n is the number of particles, m is their mass, and v is the velocity. Heat capacity of the ideal gas is

$$c_v = \frac{dE}{dT} = 3/2nk_B \quad (\text{A2})$$

If there is a gradient of the temperature in a metal, there is a flow of the electrons with the increased velocity, directed toward the low temperature (say along the x -axis). The temperature gradient produces a drift with the average velocity of

$$v_v = -\tau \frac{d}{dx} \left(\frac{v_x^2}{2} \right) \quad (\text{A3})$$

where τ is the time between collisions of particles (relaxation time) and v_x^2 is the square of the velocity along axis x ,

$$v_x^2 = 1/3v^2 \quad (\text{A4})$$

Equation (A3) can be rewritten as

$$v_v = -\frac{\tau}{3} \frac{d}{dT} \left(\frac{v^2}{2} \right) \cdot \text{grad}T \quad (\text{A5})$$

This drift will result in the changes in the density of electrons. This, in turn, will produce an electric gradient in the opposite direction with the counter-drift

$$v_E = -\frac{eE\tau}{m} \quad (A6)$$

where E is the electrostatic intensity. In equilibrium, the drifts compensate each other, and from the equality

$$v_V + v_E = 0; \quad -\frac{\tau}{3} \frac{d}{dT} \left(\frac{v^2}{2} \right) \cdot \text{grad}T = \frac{eE\tau}{m} \quad (A7)$$

we have

$$E = -\frac{1}{3e} \frac{d}{dT} \left(\frac{mv^2}{2} \right) \cdot \text{grad}T \quad (A8)$$

Taking into consideration Eq. (A1), we receive

$$E = -\frac{1}{3e} \frac{d}{dT} \left(\frac{E}{n} \right) \cdot \text{grad}T = \frac{1}{3en} c_v \text{grad}T \quad (A9)$$

and using Eq. (A2) for the heat capacity

$$E = -\frac{k_B}{2e} \text{grad}T \quad (A10)$$

As

$$\Delta U = \int E dx \quad (A11)$$

and

$$\Delta T = \int \text{grad}T dx \quad (A12)$$

Equation (A10) is equivalent to

$$\Delta U = -\frac{k_B}{2e} \Delta T \quad (A13)$$

Thus, the final equation for the coefficient between ΔU and ΔT is

$$\varepsilon = -\frac{k_B}{2e} \quad (A14)$$

The Drude theory was developed in the pre-quantum period, when the heat capacity was considered to be constant and multiple to $1/2R$ (one degree of freedom). Quantum theory has introduced the correction into the energy of electrons. Now it is evaluated by using the Fermi–Dirac statistics $f(E)$ and the density of states $\rho(E)$:

$$\langle E \rangle = \int_0^\infty E \rho(E) f(E) dE \quad (A15)$$

Such an integral is calculated conventionally using the Sommerfeld expansion:

$$\begin{aligned} \int_{-\infty}^\infty H(E) f(E) dE &= \\ &= \int_{-\infty}^{E_f} H(E) dE + \sum_{n=1}^\infty a_n (k_B T)^{2n} \frac{d^{2n-1}}{dE^{2n-1}} H(E) \Big|_{E_f} \end{aligned} \quad (A16)$$

where coefficients

$$a_n = \int_{-\infty}^\infty \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) dx = \left(2 - \frac{1}{2^{2(n-1)}} \right) \zeta(2n) \quad (A17)$$

here, $\zeta(n)$ is the Riemann zeta-function. Following these evaluations, for the energy of electrons we have

$$\begin{aligned} \langle E \rangle &= \int_0^\infty E \rho(E) f(E) dE = \\ &= \int_0^{E_f} E \rho(E) dE + \frac{\pi^2}{6} (k_B T)^2 [E_f \rho'(E_f) + \rho(E_f)] + O(k_B T)^4 \end{aligned} \quad (A18)$$

Only the first term of the expansion is shown, and the rest are negligible. The energy of electrons depends on temperature as follows

$$E = E_0 + \frac{\pi^2}{6} (k_B T)^2 \rho(E_f) \quad (A19)$$

and heat capacity is

$$c_V = \frac{dE}{dT} = \frac{\pi^2}{3} k_B^2 T \rho(E_f) = \frac{\pi^2}{2} \frac{k_B T}{E_f} n k_B \quad (A20)$$

for

$$\rho(E_f) = \frac{3}{2} \frac{n}{E_f} \quad (A21)$$

We do not show here all the steps in the evaluation, only those that clarify why the emf is proportional to the temperature. Now quantum heat capacity (A20) is substituted in Eq. (A9) instead of classic one. The result is proportional to the temperature:

$$\varepsilon = -\frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{E_f} \right) \quad (A22)$$

From the course of the evaluations and explanations, the principal distinction between dynamic and thermodynamic models becomes evident. The thermodynamic model was derived from the consideration of a pair of metals. This was developed for a thermocouple (Seebeck effect). Contrary, the dynamic models consider only one metal. Both theories, classical and quantum, deal, in fact, with the Thomson effect, i.e., with the gradient of the electric charge arising in a metal under the temperature gradient.

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