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Universality of the emf of thermocouples

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ABSTRACT

Theory of thermoelectricity defines the emf of a thermocouple through the difference in the absolute thermoelectric power (S) between two metals or alloys that constitute the thermocouple. No general relationship for the $S(T)$ was found so far, because the functions differ for different thermoelectric materials, increasing and/or decreasing with temperature, changing sign, slope, etc.

We show that the emf of a thermocouple is in fact a universal function of temperature, increasing $\sim T^2$ at low temperatures and $\sim T$ at high temperatures.

1. Introduction

Theory of thermoelectricity tells us that the emf of a thermocouple consisting of two metals, A and B, arises due to the difference between the two metals in their absolute thermoelectric power (S). The voltage is generated along the temperature gradient and is to be calculated after the integration from junction 1 at temperature T_1 to junction 2 at temperature T_2 throughout two arms of the thermocouple:

$$\Delta U = \int_{x_1}^{x_2} (S_A - S_B)\nabla T \,\mathrm{d}x = \int_{T_1}^{T_2} (S_A - S_B)\,\mathrm{d}T. \tag{1}$$

Several mechanisms converting the temperature gradient into electrical gradient were supposed to exist. These are (1) diffusion of electrons [1,2]; (2) phonon drag [3,4]; (3) "phony" phonon drag [5,6]; (4) scattering of electrons by vacancies [7]; (5) scattering of electrons by impurities [8], etc. [9]. In calculating total thermoelectric voltage, one should sum all the contributions to the thermoelectric power for one metal

$$S_A = S_{A1} + S_{A2} + S_{A3} + S_{A4} + S_{A5} + \cdots \tag{2}$$

and similarly for the other metal. Thus, the emf of a thermocouple in Eq. (1) turned out to be the sum of many components from two different metals. Every contribution is a function of temperature in its own way, depending on the mechanism of the contribution and particular properties of the metal. This is the Achilles' heel of thermoelectricity. It is conventional in physics that a theory can describe the relationship among the quantities involved in the phenomenon, providing us with a "universal" equation that can be scaled against the variable (i.e., temperature in thermal properties). Unfortunately, the sum of several scaled functions with different scaling parameters, in its turn, cannot be scaled itself.

This report shows that despite all principal difficulties in the theory of thermoelectricity, "universal" temperature relationship for the emf of thermocouple does exist.

2. Absolute thermoelectric power of metals and alloys

There is no general equation for the absolute thermoelectric power of a metal. The values of $S(T)$ for copper and lead are shown in Fig. 1 [10]. These metals are the reference materials for thermoelectricity, with plenty and accurate (as accurate as possible) experimental data. Absolute thermoelectric powers are negative for both metals at extremely low temperatures. Functions $S(T)$ for copper and lead are different, and near 10 K the values for copper start to increase with temperature. Absolute thermoelectric power of copper is positive above 50 K, while that of lead remains negative over the whole temperature range. It is impossible to describe such dissimilar functions $S(T)$ with a common (universal) function.

However, in industry thermocouples are used that are made of alloys rather then pure metals. Absolute thermoelectric power of copper, platinum, chromel, and alumel are shown in Fig. 2 [11]. All these materials are used in thermocouples in different combinations with other metals and alloys. Besides, platinum is the third

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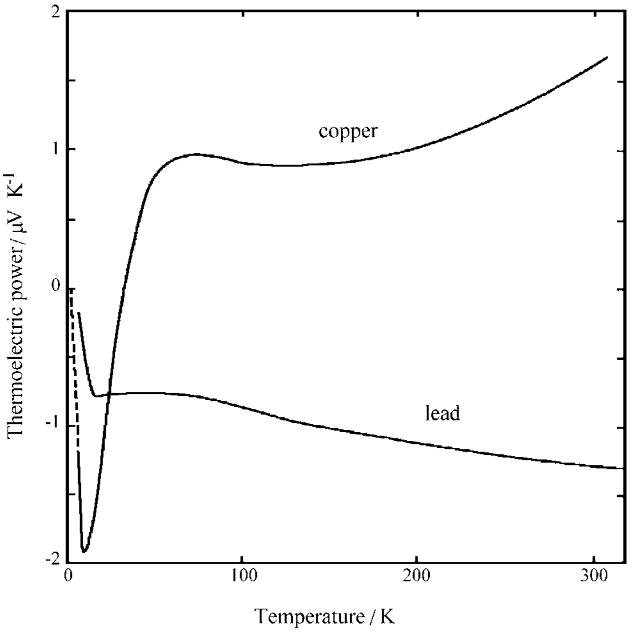

Fig. 1. Low-temperature absolute thermoelectric power for copper and lead [10].

reference material in thermoelectricity, like copper and lead. Thermoelectric power is negative for alumel and platinum, and their curves are shown in the figure as $-S(T)$. We see again dissimilar functions that cannot be described with a universal function.

Such a situation is very uncomfortable. Theory of thermoelectricity does not provide us even with a rough equation describing the absolute thermoelectric power as a function of temperature. In searching for any solution to the problem, the attempt was made to classify the S functions of transition metals according to their shape on the plot S vs. T [12]. The idea was based on the well-known similarity in physical and chemical properties among the neighbor elements in the periodic table. Twenty-five metals from eight groups were analyzed and the conclusion was made that the metals inside each group are similar in shape of the thermoelectric power vs. temperature. Unfortunately, this is not a quantitative result. The similarity was found only in the shape, not in the values. This approach was not developed afterwards and no attempt to discover the similarity has been published since then. Moreover, after the review of three transport properties (electric resistivity, thermal conductivity, and thermoelectric power) it was concluded that there is no solid theoretical framework for the quantitative explanation of these properties of transition metals. The $S(T)$ curves in Fig. 3 illustrate "jigsaw puzzle difficult even in its qualitative aspects" [13].

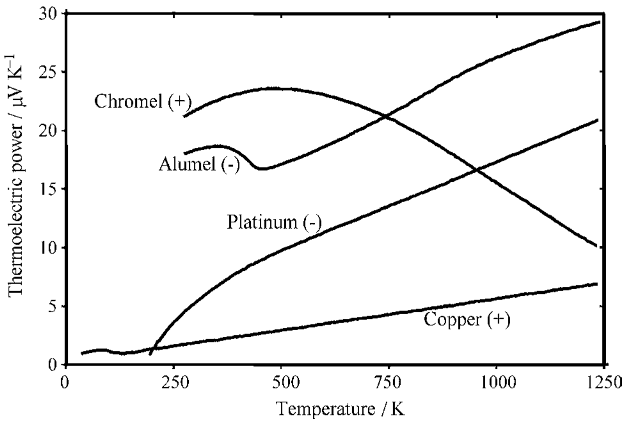

Fig. 2. High-temperature absolute thermoelectric power for copper, platinum, chromel, and alumel [11].

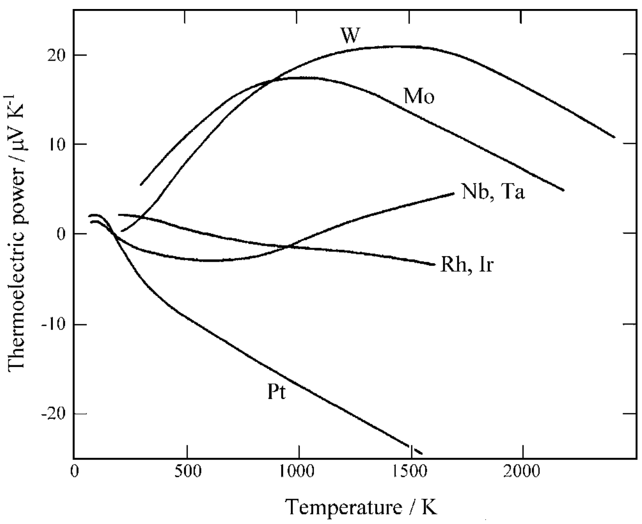

Fig. 3. Thermoelectric power for several transient metals [13].

3. The emf of thermocouples

Thermocouples are widespread tools for the temperature measurements. In industry and science, the emf is never calculated after Eq. (1), but always measured directly. Conventional way of the emf presentation is the tables with the increment of 1 °C. Corrected to the International Temperature Scale of 1990 (ITS-90), they can be downloaded for free from the site of the NIST (http://srdata.nist.gov/its90/main/). At the very beginning of thermoelectricity, the emf was considered to be the function fitted to the quadratic polynomial

$$\Delta U(\Delta t) = a_0 + a_1 \Delta t + a_2 \Delta t^2, \tag{3}$$

where Δt is the temperature difference between two junctions of the thermocouple ($\Delta t = T_2 - T_1$); and a_i are the polynomial coefficients. Quadratic polynomial was deduced from the theory of neutral temperature as the best function for the emf approximation [14]. Today, such a primitive equation cannot provide us with the accurate presentation of the emf data over a wide temperature range. Theory of thermoelectricity does not suggest new optimal function for the approximation of the emf and the tabulated data are usually fitted to the conventional polynomial of high order

$$\Delta U = \sum_{i=0}^{n} a_i t^i, \tag{4}$$

where t is the temperature in Celsius. The polynomials for all letter-designated thermocouples can also be downloaded for free from the site of the NIST (http://srdata.nist.gov/its90/main/). Reference junction of the thermocouple is to be at temperature $t = 0$ °C. To make the approximation more accurate, the whole temperature range tabulated is divided into several intervals with their own polynomials. This technical operation is proceeded without solid scientific background, according to the conventions among metrological services, or, in other words, at will. For example, the emf for thermocouple R (Pt/Pt–13% Rh) is tabulated from −50 to 1768.1 °C. It is approximated with three polynomials in the intervals: −50 to 1064.18, 1064.18–1664.5 and 1664.5–1768.1 °C. Thermocouple J (Fe/constantan) is tabulated from −210 to 1200 °C and

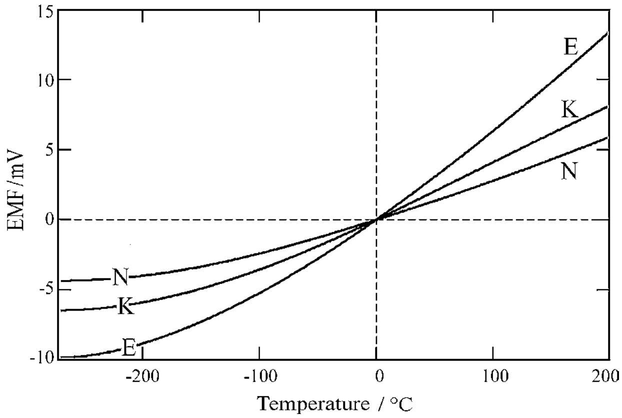

Fig. 4. The emf for thermocouples E, K, and N.

approximated with two polynomials, −210 to 760 and 760–1200 °C. Thermocouple T (Cu/constantan) is tabulated from −270 to 400 °C and approximated with two polynomials, −270 to 0 and 0–400 °C. The order of the polynomials is rather high. The powers n in Eq. (4) are 9, 5, and 4 in the three polynomials for thermocouple R; 8 and 5 in two polynomials for thermocouple J; 14 and 8 in two polynomials for thermocouple T [15,16]. Thus, the polynomial approximation of the emf of thermocouples is completely technical procedure, without any relations among polynomials for different thermocouples or even different temperature intervals of the same thermocouple. Such a procedure does not imply the similarity in the emf of different thermocouples.

The emf vs. temperature for three letter-designated thermocouples is shown in Fig. 4. In contrast to the absolute thermoelectric power of individual metals and alloys in Figs. 1–3, the emf in Fig. 4 is a smooth increasing curve. The curves for three thermocouples look very similar. They all meet at point $t = 0\,^\circ\mathrm{C}$, because this is the temperature of the reference junction. In considering physical models, one should use thermodynamic temperature (in K) rather than technical one (in °C). The emf for five thermocouples with the reference junctions at absolute zero is shown in Fig. 5. The values increase with temperature faster than the linear function.

To define the power function of temperature for the emf, we plot $\ln(\Delta U)$ vs. $\ln(T)$ (Fig. 6). All the lines are nearly parallel with one another, fitting at low temperatures to a straight line

$$\ln(\Delta U) = a + b\ \ln(T). \tag{5}$$

Tabulated data agree with the fitting function very well at low temperatures, but the slope of the curves decreases at very high temperatures. In following Vedernikov's search [12] for the similarity in the shape of experimental thermoelectric curves, one can state that the similarity does exist in the emf of thermocouples. The similarity can be expressed in formulas

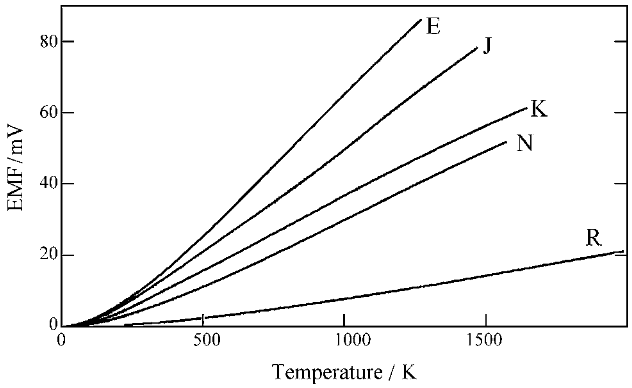

Fig. 5. The emf for five thermocouples as if the reference junctions is at absolute zero.

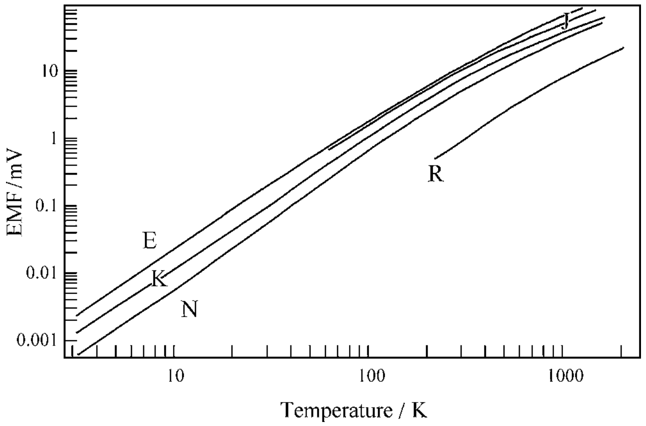

Fig. 6. Similar shape in the emf for the five thermocouples (as in Fig. 5).

$$\Delta U \sim CT^n, \tag{6}$$

for low temperatures and

$$\Delta U \sim AT \tag{7}$$

for high temperatures. In Eq. (6), $C = \exp(a)$ and $n = \exp(b)$, where a and b are the coefficients of Eq. (5). The exponent in Eq. (6) is some less than 2 (about 1.9).

The similarity in the emf curves should be considered an unexpected result. After analysis of the data on the absolute thermoelectric power (see above), we know that they cannot be fitted to a universal function for individual metals and alloys. Surprisingly, joining one metal or alloy with another one, we receive the couple generating the emf that can be expressed with a universal relationship. It is very interesting whether the materials in the thermocouples are in fact selected in such a way that the sum of two absolute thermoelectric powers for the materials fits exactly to the smooth universal function. We failed to found such a criterion for the selection of metals and alloys for thermocouples in literature.

Alternative explanation for the similarity in the temperature functions between various thermocouples was suggested in [17]. The emf was considered to arise not due to the difference in the absolute thermoelectric power derived from the Thomson coefficient, but due to the flow of electrons from one metal to the other at the contact of two dissimilar metals (the Volta effect) [18,19]. Instead of the integration along the temperature gradient throughout the whole conductor from one junction to the other, the voltage at the junction is calculated according to expression

$$\Delta U = \frac{k_B}{e}\left(T - \Theta\ \ln\left(1 + \frac{T}{\Theta}\right)\right), \tag{8}$$

where k_B is the Boltzmann constant, e is the elementary charge, and Θ is the characteristic temperature of the thermocouple, which depends on the difference in electronic heat capacity between two metals. Low-temperature expansion of the expression (8) is

$$\Delta U = \frac{k_B}{e}\left(\frac{1}{2}\frac{T^2}{\Theta} - \frac{1}{3}\frac{T^3}{\Theta^2} + \cdots\right). \tag{9}$$

In comparing Eqs. (6) and (9), one can see that the different values of Θ explain the different values of C for different thermocouples, and the negative term with T^3 makes the exponent n in the fitting expression slightly less than 2.

4. Conclusions

Every thermoelectric material has its own function $S(T)$ (negative, positive, decreasing, increasing, changing its sign in different temperature ranges). Absolute thermoelectric powers of individual metals and alloys cannot be fitted to a common function of temperature. Neither such a universal function, nor even rough empirical expression was defined so far.

The emf of thermocouples increases with temperature. The increase is nearly proportional to T^2 at low temperatures and T at high temperatures.

Without going into the discussion of the mechanism of the emf generation, we may conclude that the emf of thermocouples obeys the universal temperature function. This fact can be very useful in thermoanalytical practice, for example, for the optimal fitting of the emf to polynomials [20].

References

[1] A. Sommerfeld, N.H. Frank, Rev. Mod. Phys. 3 (1931) 1.
[2] J.M. Ziman, Electrons and Phonons, Oxford University Press, 1960, p. 403.
[3] L. Gurevich, J. Phys. (USSR) 9 (1945) 477.
[4] L. Gurevich, J. Phys. (USSR) 10 (1946) 67.
[5] P.E. Nielsen, P.L. Taylor, Phys. Rev. Lett. 21 (1968) 893.
[6] P.E. Nielsen, P.L. Taylor, Phys. Rev. B 10 (1974) 4061.
[7] J.F. Blatt, Phys. Rev. 100 (1955) 666.
[8] J. Friedel, Philos. Mag. 43 (1952) 153.
[9] J.F. Blatt, P.A. Schroeder, C.L. Foiles, D. Greig, Thermoelectric Power of Metals, Plenum Press, New York/London, 1976.
[10] R.H. Kropschot, J.F. Blatt, Phys. Rev. 116 (1959) 617.
[11] R.R. Heikes, R.W. Ure Jr., Thermoelectricity: Science and Engineering, Interscience Publishers, New York/London, 1961, p. 313.
[12] M.V. Vedernikov, Adv. Phys. 18 (1969) 337.
[13] G.K. White, Aust. J. Phys. 46 (1993) 707.
[14] B.S. Finn, Adv. Electron. Electron Phys. 50 (1980) 175.
[15] GOST 3044-84, Thermocouples, Gosstandart SSSR, Moscow, 1989, p. 79.
[16] http://srdata.nist.gov/its90/main/.
[17] V.A. Drebushchak, J. Therm. Anal. Calorim. 90 (2007) 289.
[18] H.C. Burbridge, Phys. Rev. 2 (1913) 183.
[19] W.R. Harper, Proc. R. Soc. Lond. A 205 (1951) 83.
[20] V.A. Drebushchak, J. Therm. Anal. Calorim. 96 (2009) 315.