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Theory of Electricity by Rudolf Clausius in the Development of Thermodynamics

Abstract

Clausius's four papers (1852-57) on the theory of electricity are analyzed by the help of our own database. These papers are classified by him under the mechanical theory of heat together with his papers on thermodynamics and gas theory. The first law and the essential part of the second law of thermodynamics were established in his first *Abhandlung* (1850). The first law is applied to these four papers on the theory of electricity, where heat, produced by electricity, is considered as the equivalent with the mechanical work. The essential part of the second law is applied to the 12th paper on thermoelectric current. The current between two different metals is treated by the similar method to heat flow. Here the temperature dependence is expressed as *dt/C* which is the maximum work of the infinitesimal Carnot cycle.

1. Introduction

R. Clausius's published papers, books (1847-85) and his manuscripts at the Library of the Deutsches Museum were studied,[9-16] and the role of his papers on the theory of electricity was made clear. The so called "Clausius's mechanical theory of heat" (*die Mechanische Waermetheorie*) consists of three fields, e.g., thermodynamics, the theory of electricity, and gas theory. Two volumes of his collected papers, compiled his 16 papers.[1] Among these 16 papers, the 1st to the 9th papers (1850-65) are on thermodynamics, the 10th to the 13th papers (1852-7) on the theory of electricity, and the 14th to the 16th papers (1857-62) on gas theory.[2]

Clausius presented the first law of thermodynamics in his first paper on the mechanical theory of heat in 1850,[2(I)] in the differential form. After that, in his 4th paper in 1854,[2(IV)] Clausius proposed the (pre) second law for the reversible process in the similar differential form. Then, he treated these two laws as a set of equations. In his 9th (1865) paper,[2(IX)] Clausius presented the first and second laws of thermodynamics for both reversible and irreversible processes by the differential equations and by the following well-known literary expressions:

[1] CLAUSIUS (1864)
[2] See a list of Clausius's 16 papers (I–XVI).

The first law: *The energy of the universe is constant*,
The second law: *The entropy of the universe tends to a maximum*.

In our paper at the Conference, Volta and the History of Electricity, the roles of above papers by Clausius on the theory of electricity will be discussed in connection with studies on thermodynamics and gas theory in detail. There are few papers along this line yet.

2. Clausius Four Papers on the Theory of Electricity

In this section, the contents of Clausius's four papers on the theory of electricity will be discussed.

The first one was the Xth *Abhandlung*,[2(X)] published in 1852, (*On the mechanical equivalent between electric discharge and heat produced by it on the leading wire*). Here Clausius applied the theory of equivalent between heat and mechanical work to electrical heat. The theory of equivalent is the essential part of the first law of thermodynamics, established in his first paper on thermodynamics in 1850, e.g., the first *Abhandlung*. Clausius's viewpoint that heat is produced by motions of the smallest parts of matter, made it possible for him to treat electrical heat.

The second paper was the XIth *Abhandlung*,[2(XI)] published in 1852, (*On the work made by a stationary electrical current on the leading wire, and the heat produced*). Here Clausius obtained theoretically Joule's law from Ohm's law by the use of the above theory of equivalent between heat and mechanical work.

The third paper was the XIIth *Abhandlung*,[2(XII)] published in 1853, (*On the application of the mechanical theory of heat to the thermoelectric phenomena*). Here Clausius also discussed the movements of small particles, which produce heat. The theory of equivalent was applied together with Carnot's function, which includes a part of the second law of thermodynamics. This paper will be discussed in detail in the other independent section because it is the most important among Clausius's papers on the theory of electricity, which has the applications of both the first and second laws.

The fourth paper was the XIIIth *Abhandlung*,[2(XIII)] published in 1857, (*On the electrical current during electroanalysis*). Here Clausius also used the theory of equivalent with the particle theory of matter.

3. Mathematical Preparation by Clausius

In Clausius's collected papers, mentioned above, entitled *Abhandlungen ueber die Mechanische Waermetheorie, Zweite Abtheilung*, 1867,[3] there was a mathematical introduction, called *Einleitungen in die mathematische Behandlung der Electricitaet* (written in 1866) compiled in the previous part of those 4 papers on the theory of electricity. Here Clausius summarized George Green's work, published in 1828. This

[3] CLAUSIUS (1867), "Zweite Abtheilung", pp. 59-97.

paper by Green is known as the paper where the term *potential function* was first introduced.[4] Green presented the mathematical theory of electricity, following after Poisson. The potential function V indicated by Green as the integral of the quantity of electricity of a particle divided by the distance between the particle and a given point. (Yagi appreciates Prof. Ivor Grattan-Guinness' useful suggestion on Green's potential function).[5] It is worth pointing out that at the Library of the Deutsches Museum there exists Clausius's manuscript HS 6426, which is a dark blue color notebook, entitled *Verleitung Electricitaet nach Poisson* as the record of Clausius reading Green's work together with that of Poisson between 1851 and 1852. In the above mathematical introduction Clausius referred to Green, and wrote the same potential function V, which was used in all his papers on the theory of electricity, namely, in the Xth *Abhandlung*, the XIth, the XIIth, and the XIIIth.

4. Clausius's First and Second Laws of Thermodynamics Applied to the Theory of Electricity

Here the *XIIth Abhandlung*, on the application of the mechanical theory of heat to the thermoelectric current, will be discussed. This paper was delivered at the Berlin Academy in November, and published in the *Annalen*, December of 1853. According to Peltier, Clausius started to study the situation between two kinds of different material. By expressing the electrical difference between each potential function as E, Clausius wrote the following equation: $E = V2 - V1$ (p. 176). Clausius assumes that heat is produced by the potential difference, which causes a molecular movement (that he calls heat), e.g., the electric charge moves from one material to the other material by the corresponding force, acting between these two metals (p. 178). The mechanical work W, done in a unit of time, indicated by E multiplied by J which is the amount of electric charge:

$$W = E\,J$$

and the corresponding heat H, is shown by the next equation:

$$H = A\,E\,J,$$

where "A" is Clausius's constant, called the equivalent of heat for the unit of mechanical work (p. 184). This is the application of the theory of equivalent between heat and mechanical work (the first law) to the theory of electricity.

In addition to the first law, the temperature dependence was discussed by Clausius by the use of Carnot's function C (the essential part of the second law) (p. 192).

$$\text{The work produced / the heat transmitted} = dt/C$$

where dt indicates the temperature difference between two metals. Replacing $A\ (a+t)$

[4] GREEN (1828), p. 5.
[5] GRATTAN-GUINNESS (1995).

for the function *C*, Clausius obtained the value of *E*:

$$E = e\,(a + t),$$

where *e* is a constant, depending on the above two metals.

It is worth pointing out that Clausius's fundamental way of approach, developed in his first paper on thermodynamics[2(I)], was applied, as mentioned above, to his 12th paper on the theory of electricity. Clausius wrote in the *first Abhandlung:*[2(I)]

The heat expended / the work produced = A

where "*A*," is Clausius's constant, called *the equivalent of heat for the unit of work*, [English trans. p.27], more briefly, *the calorific equivalent of work* [the foot note, English trans. p.27]. Further, Clausius wrote the maximum work by the infinitesimal Carnot cycle in the latter part of the same paper. The maximum work, effected by the transmission of a unit of heat from body *A* at temperature *t* to the body *B* at temperature $t + dt$, is expressed by dt/C.

Presently, the studies on the thermoelectric phenomenon are mentioned under such two pioneer names as Jean Peltier and William Thomson. Namely, Peltier is the person who discovered the Peltier effect. W. Thomson found the temperature dependence of the effect. For example, they are referred to in "Rikagaku-jiten," a famous dictionary of physics and chemistry[†], and "A Physicist's Desk Reference, the Second Edition of Physics Vade Mecum".[‡]

5. William Thomson's Evaluation on Clausius's Studies

Thomson began to take interest in this subject through Joule between 1843 and 1847. In a paper on the mechanical theory of thermo-electric currents,[6] published December, 1851 (which is compiled in Thomson's collected papers), Thomson referred to the Peltier discovery. Namely, heat is absorbed at a surface in a compound metallic conductor when electricity traverses from bismuth to antimony. On the other hand, heat is generated when the electricity traverses in the contrary direction, i.e., from the antimony to the bismuth. Thomson presented a fundamental equation to indicate the heat generated for the unit of time. The equation has two kinds of terms: The first one is based on the theory of equivalence between heat and mechanical work (the first law of thermodynamics), where Thomson uses Joule's *J*, which is $1/A$, the mechanical equivalent for heat. The second term includes temperature dependence. Here Thomson applied the principle of heat to the case of electrical current. The principle, Thomson wrote, "first enunciated by Carnot and first established in the dynamical theory by Clausius".[7] Although Thomson was not completely satisfied with the

[†] Published by Iwanami Shoten publishers, Tokyo, 5th ed., 1998, p. 1017.
[‡] Published by the American Institute of Physics, New York, 1989, p. 310.
[6] THOMSON (1851).
[7] *Ibid.*, p. 318.

analogy between heat and electric current, he used Carnot's function to express the above second term. (Note that Thomson did not use "*C*" for the expression of Carnot's function but rather used "1/ *u*(*mu*)" in his own equation).

Clausius himself referred to Thomson's work on the thermoelectric current in the 12th paper. Here Clausius emphasized the importance of the use of "potential function" to this subject, which Thomson did not.

6. Findings through a Database and the Nature of our Database

We created a simple type of database (1st edition[8] in 1989, 2nd edition[9] in 1998) which is only a list of about 500 equations, arranged under Clausius's 16 papers. Having studied Clausius's mechanical theory of heat by the use of our database, we drew a few stimulating findings, and this proved that such a simple type of database is worth making. Just looking through these equations, we could recognize Clausius's pairing attitude toward the first and second laws of thermodynamics. And the equation with Carnot's function in the paper on the theory of electricity was found out. These findings are greatly due to the ability to glance through the database.

Being able to quickly scan through the equations revealed two different unit expressions for the first law of thermodynamics by Clausius. Namely, he wrote the first law on the unit of heat using "*A*" in his papers on thermodynamics and the theory of electricity. On the other hand, the unit of mechanical work was adopted using "1/*A*" in those papers on gas theory. Here "*A*" is Clausius's constant, the equivalent of heat for the unit of work, or the calorific equivalent for work.

In the 1st edition of Clausius's database, as mentioned, we aimed to make a list of his equations included in his 16 papers. We made the 1st edition using MacWrite™ and TECH™ font on our Macintosh Plus™. We would have planned to use the TeX[10] format from the beginning. However, we did not have the proper environment. Our Macintosh needed more power to use the TeX software. For example, it was difficult to describe any fraction by this way. Although the form "*a*/*b*" was mostly used rather than the original historical form, we obtained a useful list to glance at these equations.

In the 2nd edition, we prepared a better environment for the TeX on our new Macintosh™. By using the TeX, Clausius's equations could be written in the original historical form. The capability to use other kinds of computer hardware and software was increased. So we are on the way to creating an ideal database.

7. Remarks and Conclusions

R.Clausius's published papers, books (1847-85) and his manuscripts at the Library of the Deutsches Museum, were studied using our database, and the role of his papers on

8 YAGI (1989).
9 YAGI (1998).
10 KNUTH (1984).

the theory of electricity was made clear. Namely, the theory of electricty has an important position in Clausius's mechanical theory of heat because the mechanichal theory itself consists of the theory of electricity together with thermodynamics and gas theory. Clausius's important contribution to thermodynamics was published in his first paper on thermodynamics in 1850. Here he modified Carnot's material theory of heat for the mechanical theory. The first law of thermodynamics was expressed by Clausius in a differential form with Clausius's constant A (the calorific equivalent for work). The heat expended by the infinitesimal Carnot cycle was considered as the second order differential where Carnot's principle was included as the first order differential.[11] The second law of thermodynamics was presented along the line of Carnot, which had already been expressed mathematically by Clapeyron. Here Clausius wrote the maximum work of the cycle as dt/C where "C" is the Carnot function.

In Clausus's four papers on the theory of electricity, the first and second laws are applied to solve electrical phenomena, as mentioned above. Through these applications Clausius's mechanical theory of heat was well established. The way of approach to assume small particles of matter was also developed in these four papers by Clausius. The particle theory was fully used in his later papers on gas theory, publication of which started in 1857.

[11] YAGI (1984).

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NOTE
A list of R.Clausius's publications was made by Yagi in Ref. 12) in 1990. A copy of another list of his publications, called 'Verzeichniss der wissenschhaftlichen Veroeffentlichungen von Clausius,' with "Rede" by Eduard Riecke (Dieterichsche Verlags-Buchhandlung, Goettingen, 1888), was kindly given to Yagi by the librarian of Burnday Library, Dibner Institute during her stay there in the summer of 1994.