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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

# On the Relationship between Heat Exchanges and Temperature of Bodies at Thermal Equilibrium

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**Abstract**—The paper refers first to the definition of heat prevalent in thermodynamics. The problem of the temperature and of the exchanges of heat in the bodies at thermal equilibrium is then addressed, providing a new point of view based on the principle of mobile equilibrium.

**Keywords:** thermodynamics, equilibrium, heat exchange

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## 1. NUDA NOMINA TENEMUS

Compared to all the others physical quantities of which we become aware during our university studies, heat is perhaps the one of which we have also, from the first days of life, both a physical and psychological perception. In common language, the word "heat" has several meanings and it is not surprising that, even in thermodynamics, there is or there was a variety of interpretations to explain it. The rationalization of the concept of heat was only possible after the invention of the thermometer and when it was understood that heat and temperature are not synonymous. In the scientific literature, several papers retrace the steps that led from the caloric to the transfer of energy between bodies having different temperatures [1–5]. The current prevailing idea is that heat is not an intrinsic property of the system but it is energy transferred from one body to another one due to a temperature difference. The ambiguities should be resolved once we use the concept of internal energy and we refer to heat Q and work W as methods to produce changes of internal energy [6]. An even more drastic position would like the terms heat and work to be discarded from thermodynamics. The caloric era ended around the middle of the XIX century, but by using the word heat we simply changed the ambiguity without eliminating it [7]. However, as Lewis and Randall wrote many years ago: "There are two terms, heat and work, that have played an important part in the development of thermodynamics, but their use often brought an element of vagueness into a science capable of the greatest precision, it is not, however, convenient to avoid altogether the use of these terms" [8].

## 2. HEAT EXCHANGE IN THE BODIES AT THERMAL EQUILIBRIUM

At the end of the XVIII century, Pierre Prévost wrote a memoir in which he established the principle of heat exchanges or principle of mobile equilibrium for radiant heat [9]. Bodies of different nature and at different temperatures, contained in a cavity at constant temperature T, after a finite time attain the temperature of the cavity. Once thermal equilibrium is reached, the bodies do not cease to emit and absorb thermal radiation, but the exchanges persist incessantly.

Between the end of the XVIII century and the middle of the XIX century, heat exchanges were described in terms of the caloric, a supposed fluid transporting heat. Caloric does not exist and the word caloric gradually lost its meaning and was used less and less, but the problem of understanding by which laws heat is transmitted between bodies at different temperatures remained on open issue.

In the first two decades of the XIX century, Joseph Fourier founded the new science of heat exchanges by conduction. Fourier [10] based his analysis on Prevost's principle, by considering it as the regulating principle of heat exchanges. Between two bodies in mutual contact there is a net heat exchange ("simple" in Fourier's words) which is equal to the difference between the quantity of heat flowing from A to B and that from B to A. According to Fourier the net heat had no physical meaning but the only meaningful quantity is the heat transferred from A to B and that from B to A. It was not possible to give an expression to these individual heat amounts, but it was possible to

provide a formula for the net heat flow $J$ between two bodies at different temperatures [14]

$$J_{\text{net}} = \alpha(T_{\text{A}} - T_{\text{B}}). \quad (1)$$

In 1879, Josef Stefan found the correct formula that relates the quantity of energy emitted by thermal radiation from a blackbody and the fourth power of its absolute temperature [11]. The formula was theoretically demonstrated by Ludwig Boltzmann by using the laws of thermodynamics (1879), on the basis of a thermodynamic cycle conceived by Adolfo Bartoli (1876) to justify the existence of a pressure associated with thermal radiation [12, 13]. The Stefan–Boltzmann formula can be written as follows by using the intensity of radiation or radiation flux density $J$ ($\pi I$ in [14], J m$^{-2}$ s$^{-1}$)

$$J = \frac{1}{4}\left(\frac{U}{V}\right)c, \quad (2)$$

where $J$ depends on the energy density $U/V$ of the blackbody radiation, with $V$ the cavity volume, and on the velocity of light $c$. Formula (2) can be rewritten as

$$J = \frac{1}{4}\left(\frac{U}{VT}\right)Tc. \quad (3)$$

The Fourier's reasoning, in the light of Prévost's principle, leaves open the following problem: how much heat does flow back and forth from any region inside a homogeneous body in thermal equilibrium? We can generalize (2) and (3) for any quantity that homogeneously fills the space and propagates with velocity $v$ in all directions

$$J = \frac{1}{4}\left(\frac{U}{VT}\right)Tv. \quad (4)$$

The dependence of $\phi(T) = U/VT$ on temperature and other physicochemical quantities is related to the physical mechanism underlying the energy transfer. Let's consider three mechanisms for energy transfer, thermal radiation (photons, bosons), lattice vibrations (phonons, bosons), and free electrons (fermions) in a metal.

### *2.1. Blackbody Radiation*

The radiant flux density is given by

$$J = \frac{1}{4}\phi(T)Tc.$$

The energy density of the blackbody radiation or thermal radiation is given by

$$\frac{U}{V} = \beta T^4,$$

where $\beta = 7.57\times10^{-16}$ J m$^{-3}$ K$^{-4}$. Hence

$$J = \frac{1}{4}\beta T^3 Tc.$$

The entropy per unit volume $S/V$ of thermal radiation is

$$\frac{S}{V} = \frac{4}{3}\beta T^3.$$

The term $\phi(T) = \beta T^3$ is of the same order of the number of photons, i.e., the excitable quanta that carry the energy, and it is also of the same order of magnitude of the entropy of thermal radiation.

### *2.2. Lattice Vibrations (Debye)*

According to the Debye model, the phonon energy in a solid composed by $N$ identical atoms is given by [15, 16]

$$U = \frac{9}{8}Nk\theta_{\text{D}} + 9NkT\left(\frac{T}{\theta_{\text{D}}}\right)^3\int_0^{x_{\text{D}}}\frac{x^3}{e^x-1}dx,$$

where $\theta_{\text{D}}$ is the Debye characteristic temperature and $x_{\text{D}} = \theta_{\text{D}}/T$. The first term $\frac{9}{8}Nk\theta_{\text{D}}$ is the ground state energy of the system or zero-point vibrational energy $U_0$.

Hence

$$\frac{U-U_0}{V} = 9\frac{Nk}{V}T\left(\frac{T}{\theta_{\text{D}}}\right)^3\int_0^{x_{\text{D}}}\frac{x^3}{e^x-1}dx.$$

The phonon flux density within the solid can be written as

$$J = \frac{1}{4}\phi(T)Tv_s,$$

where

$$\phi(T) = \frac{U-U_0}{V}\frac{1}{T} = 9\frac{Nk}{V}\left(\frac{T}{\theta_{\text{D}}}\right)^3\int_0^{x_{\text{D}}}\frac{x^3}{e^x-1}dx$$

and $v_s$ is the sound velocity, $V$ the volume at temperature $T$. The phonon entropy per unit volume in the Debye model is given by

$$\frac{S}{V} = 9\frac{Nk}{V}\left(\frac{T}{\theta_{\text{D}}}\right)^3\left[\int_0^{x_{\text{D}}}\frac{x^3}{e^x-1}dx - \int_0^{x_{\text{D}}}x^2\ln(1-e^{-x})dx\right].$$

### *2.3. Lattice Vibrations (Einstein Model)*

According to the Einstein model, the phonon energy in a solid composed by $N$ identical atoms is given by

$$U = \frac{3}{2}Nk\theta_{\text{E}}\frac{1+\exp\left(-\frac{\theta_{\text{E}}}{T}\right)}{1-\exp\left(-\frac{\theta_{\text{E}}}{T}\right)}.$$

By subtracting the zero-point vibrational energy $U_0 = U(T\to0) = \frac{3}{2}Nk\theta_{\text{E}}$ we have

$$U - U_0 = 3Nk\theta_E \frac{\exp\left(-\frac{\theta_E}{T}\right)}{1-\exp\left(-\frac{\theta_E}{T}\right)}.$$

Hence the phonon flux density is

$$J = \frac{1}{4}\phi(T)Tv_s,$$

where

$$\phi(T) = \frac{U-U_0}{V}\frac{1}{T} = 3\frac{Nk}{V}\left(\frac{\theta_E}{T}\right)\frac{\exp\left(-\frac{\theta_E}{T}\right)}{1-\exp\left(-\frac{\theta_E}{T}\right)}.$$

The phonon entropy per unit volume is

$$\frac{S}{V} = 3\frac{Nk}{V} \times \left\{\left(\frac{\theta_E}{T}\right)\frac{\exp\left(-\frac{\theta_E}{T}\right)}{1-\exp\left(-\frac{\theta_E}{T}\right)} - \ln\left[1-\exp\left(-\frac{\theta_E}{T}\right)\right]\right\}.$$

### *2.4. Free Electrons*

The energy density of free electrons in [16]

$$\frac{U}{V} = \frac{3}{5}\mu_0\frac{N_e}{V}\left[1+\frac{5}{12}\left(\frac{\pi kT}{\mu_0}\right)^2\right],$$

where $N_e$ is the number of free electrons, and $\mu_0$ is the Fermi level of electrons at 0 K

$$\mu_0 = \frac{h^2}{8m}\left(\frac{3N_e}{\pi V}\right)^{2/3}.$$

By subtracting the term independent from temperature we obtain

$$\frac{U-U_0}{V} = \mu_0\frac{N_e}{V}\frac{1}{4}\left(\frac{\pi kT}{\mu_0}\right)^2.$$

The entropy per unit volume of the free electron gas is given by

$$\frac{S}{V} = \frac{\pi^2 k}{2}\frac{N_e}{V}\left(\frac{kT}{\mu_0}\right).$$

The free electron flux density is given by

$$J = \frac{1}{4}\phi(T)Tv_F,$$

where

$$\phi(T) = \left(\frac{U}{V} - \frac{3}{5}\mu_0\frac{N_e}{V}\right)\frac{1}{T},$$

and $v_F$ is the Fermi velocity of electrons.

## 3. NUMERICAL EXAMPLES

Let's calculate the flux density of blackbody radiation, and the flux density of lattice vibrations and free electrons in solid copper taken as representative metal. In all cases the temperature is $T = 298.15$ K.

Data for copper: Debye temperature $\theta_D = 315$ K, Einstein temperature $\theta_E \cong 0.775\theta_D = 244$ K, molar volume $\underline{V} = 7.11\times10^{-6}$ m$^3$/mol, sound velocity $v_s = 3678$ m/s,[1] free electron density $N_e/V = 8.47\times10^{28}$ m$^{-3}$ and the Fermi velocity $v_F = 1.570\times10^6$ m/s.

### *3.1. Blackbody Radiation*

$$\frac{U}{V} = 7.57\times10^{-16}\times(298.15)^4 = 5.978\times10^{-6}\ \frac{\text{J}}{\text{m}^3},$$

$$\phi(T) = \frac{5.978\times10^{-6}}{298.15} = 2.005\times10^{-8}\ \frac{\text{J}}{\text{m}^3\ \text{K}},$$

$$J = \frac{1}{4}\times2.005\times10^{-8}\times298.15\times3\times10^8 = 4.481\times10^2\ \frac{\text{J}}{\text{m}^2\ \text{s}},$$

$$\frac{S}{V} = \frac{4}{3}\times7.57\times10^{-16}\times(298.15)^3 = 2.674\times10^{-8}\ \frac{\text{J}}{\text{m}^3\ \text{K}}.$$

### *3.2. Lattice Vibrations Debye Model (Cu)*

$$\frac{U-U_0}{V} = 9\frac{8.314}{7.11\times10^{-6}}\times298.15\times\left(\frac{298.15}{315}\right)^3 \times0.952 = 6.897\times10^8\ \frac{\text{J}}{\text{m}^3},$$

$$\phi(T) = \frac{6.897\times10^8}{298.15} = 2.313\times10^6\ \frac{\text{J}}{\text{m}^3\ \text{K}},$$

$$J = \frac{1}{4}\times2.313\times10^6\times298.15\times3678 = 6.342\times10^{11}\ \frac{\text{J}}{\text{m}^2\ \text{s}},$$

$$\frac{S}{V} = 9\times\frac{8.314}{7.11\times10^{-6}}\times\left(\frac{298.15}{315}\right)^3\times0.514 = 4.583\times10^6\ \frac{\text{J}}{\text{m}^3\ \text{K}}.$$

[1] The value has been calculated from $v_s = 2av_E$ where $v_E = k\theta_E/h = 5.087\times10^{12}$ s$^{-1}$ and $a = 3.615\times10^{-10}$ m is the lattice parameter at 298.15 K.

**Table 1.** Calculated values of propagation velocity $v$, energy density $\phi$, entropy per unit volume $S/V$, flux density $J$ for the considered systems

| | $v\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$ | $\phi\left(\frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}}\right)$ | $\frac{S}{V}\left(\frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}}\right)$ | $J\left(\frac{\mathrm{J}}{\mathrm{m}^2\ \mathrm{s}}\right)$ |
|---|---|---|---|---|
| Blackbody radiation | $3 \times 10^8$ | $2.005 \times 10^{-8}$ | $2.674 \times 10^{-8}$ | $4.481 \times 10^2$ |
| Lattice vibrations (Debye, Cu) | 3678 | $2.313 \times 10^6$ | $4.583 \times 10^6$ | $6.342 \times 10^{11}$ |
| Lattice vibrations (Einstein, Cu) | 3678 | $2.265 \times 10^6$ | $4.304 \times 10^6$ | $6.209 \times 10^{11}$ |
| Free electrons (Cu) | $1.57 \times 10^6$ | $1.054 \times 10^4$ | $2.108 \times 10^4$ | $1.234 \times 10^{12}$ |

### *3.3. Lattice Vibrations Einstein Model (Cu)*

$$\frac{U-U_0}{V} = 3\times\frac{8.314}{7.11\times10^{-6}}\times 244\times\frac{\exp(-0.818)}{1-\exp(-0.818)} = 6.752\times10^8\ \frac{\mathrm{J}}{\mathrm{m}^3},$$

$$\phi(T) = \frac{6.752\times10^8}{298.15} = 2.265\times10^6\ \frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}},$$

$$J = \frac{1}{4}\times 2.265\times10^6\times 298.15\times 3678 = 6.209\times10^{11}\ \frac{\mathrm{J}}{\mathrm{m}^2\ \mathrm{s}},$$

$$\frac{S}{V} = 3\times\frac{8.314}{7.11\times10^{-6}}\times\left\{0.818\times\frac{\exp(-0.818)}{1-\exp(-0.818)} - \ln\left[1-\exp(-0.818)\right]\right\} = 4.304\times10^6\ \frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}}.$$

### *3.4. Free Electrons (Cu)*

$$\frac{U-U_0}{V} = 1.127\times10^{-18}\times 8.47\times10^{28}\times\frac{1}{4}\left(\frac{\pi\times1.381\times10^{-23}\times298.15}{1.127\times10^{-18}}\right)^2 = 3.143\times10^6\ \frac{\mathrm{J}}{\mathrm{m}^3},$$

$$\phi(T) = \frac{3.143\times10^6}{298.15} = 1.054\times10^4\ \frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}},$$

$$J = \frac{1}{4}\times1.054\times10^4\times298.15\times1.570\times10^6 = 1.234\times10^{12}\ \frac{\mathrm{J}}{\mathrm{m}^2\ \mathrm{s}},$$

$$\frac{S}{V} = \frac{\pi^2}{2}\times1.381\times10^{-23}\times8.47\times10^{28}\times\frac{1.381\times10^{-23}\times298.15}{1.127\times10^{-18}} = 2.108\times10^4\ \frac{\mathrm{J}}{\mathrm{m}^3\ \mathrm{K}}.$$

Table 1 summarizes the numerical results.

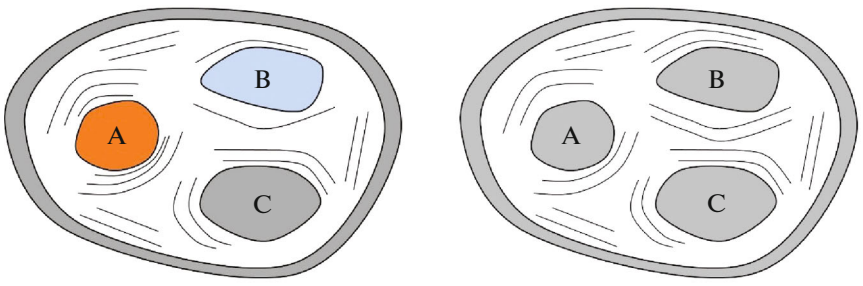


**Fig. 1.** Different bodies (A, B, C) in a cavity at constant temperature (left: beginning; right: thermal equilibrium; the different colors of the bodies schematize their temperatures).

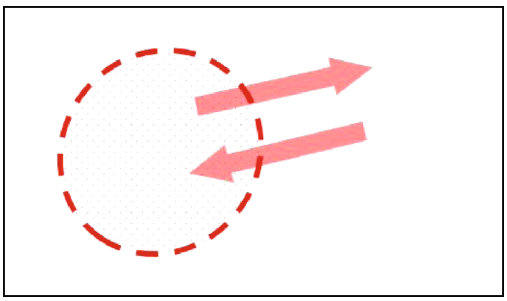

**Fig. 2.** Heat exchange in a homogeneous material (outgoing heat is equal to the incoming one).

## 4. CONCLUSIONS

The word heat encompasses several meanings, with many facets, as there are different forms of heat each of which is related to a different transfer mechanism such as thermal radiation, lattice vibrations, and conduction electrons. We could even affirm that heat does not exist and only physical mechanisms (heat as a type of motion, collective) of energy transfer exist. The different mechanisms are ranked both by the link between the transferred specific entropy and the temperature, and by the velocity of propagation. Heat flux is related to the mass and number of bodies that travel, the speed at which they move and the temperature. In this picture, temperature acquires the meaning of a measure of the tendency (tension) of a body to expel its internal energy in the form heat with the characteristic times of the different physical mechanisms. Here we calculated the flux density for thermal radiation and the value is several orders of magnitude less than the flux density both for lattice vibrations and free electrons in a solid. The reason is due to the fact that the velocity of transfer is an important factor but also the mass and the number of the moving particles. The values calculated with the harmonic crystal theory (parabolic potential between atoms, Einstein model or Debye model) are very high compared to the heat flux associated with thermal radiation in a cavity. This find a justification with the fact that a harmonic crystal has an infinite thermal conductivity. Thus, the heat flux that moves back and forth in a solid at equilibrium related to the lattice vibrations is very large.

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## CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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