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Specific Heat Capacity of Beryllium

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1. The heat capacity in the solid state

1.1. Classical approach

The starting point to describe the thermal behavior of bodies in the solid state in a classical way is the model of an ideal crystal. All atoms are fixed at a given point in the lattice at the temperature of absolute zero. They start to oscillate around their equilibrium state at $T > 0$. If interactions between the atoms are neglected, each atom behaves exactly like a harmonic oscillator. The equipartition theorem from classical statistical mechanics states that the mean energy $\bar{E}$ of any oscillator is given by

$$\bar{E} = \frac{1}{2} f \cdot k_{\mathrm{B}} T \ ,$$

where k_{B} is the Boltzmann constant and f the number of degrees of freedom. An oscillator in three dimensions has three degrees of freedom with regard to potential energy and three more with regard to kinetic energy. Therefore we have

$$\bar{E} = 3 \, k_{\mathrm{B}} T \ .$$

Introducing the Avogadro constant N_{A} we find the mean internal energy of a mole

$$U_{\mathrm{M}} = 3 N_{\mathrm{A}} \cdot k_{\mathrm{B}} T = 3 R T \ .$$

By definition the heat capacity is

$$C_V = \left(\frac{\partial U_{\mathrm{M}}}{\partial T} \right)_V \ .$$

Thus we can derive the classical law of *Dulong-Petit*

$$C_V = 3 \, R = 6 \cdot \frac{\mathrm{cal}}{\mathrm{mol} \cdot K} \ .$$

This indicates that the molar specific heat capacity should have the same – temperature independent – value for all bodies in the solid state. But experiments show that this is only true in the limit of high temperatures. Obviously, the classical model cannot account correctly for conditions at lower temperatures. Furthermore, it contradicts the third law of thermodynamics which states that C_V should tend to zero as T tends to zero.

1.2. Simple quantum mechanical model of independent oscillators

Einstein gave an explanation for the deviations from the law of Dulong-Petit in 1907: Again we assume the molecules to be independent harmonic oscillators in three dimensions. In addition we know that one oscillator that can oscillate in three different directions is equivalent to three oscillators that can only oscillate in one direction. By the laws of quantum mechanics the possible energy values for these one-dimensional oscillators are given by

$$E_n = \left(n + \frac{1}{2}\right) \cdot \hbar\omega \qquad \text{with } n = 0, 1, 2, \ldots$$

The Boltzmann mean value of the energy is thus

$$\bar{E} = \frac{\sum\limits_0^\infty E_n \cdot \mathrm{e}^{\frac{E_n}{k_\mathrm{B}T}}}{\sum\limits_0^\infty \mathrm{e}^{\frac{E_n}{k_\mathrm{B}T}}} = \frac{1}{2}\,\hbar\omega + \frac{\sum\limits_0^\infty n\hbar\omega \cdot \mathrm{e}^{\frac{n\hbar\omega}{k_\mathrm{B}T}}}{\sum\limits_0^\infty \mathrm{e}^{\frac{n\hbar\omega}{k_\mathrm{B}T}}}\ ,$$

where we have separated the zero point energy $\frac{1}{2}\,\hbar\omega$ in the second step.
Substituting $x = \frac{-\hbar\omega}{k_\mathrm{B}T}$ we have

$$\bar{E} = \frac{1}{2}\,\hbar\omega + \hbar\omega \cdot \frac{\sum\limits_1^\infty n \cdot \mathrm{e}^{nx}}{1 + \sum\limits_1^\infty \mathrm{e}^{nx}} = \frac{1}{2}\,\hbar\omega + \hbar\omega \cdot \frac{d}{\mathrm{d}x} \log\left(1 + \sum\limits_1^\infty \mathrm{e}^{nx}\right)$$

and after differentiating

$$\bar{E} = \frac{1}{2}\,\hbar\omega + \frac{\hbar\omega}{\mathrm{e}^{\frac{\hbar\omega}{k_\mathrm{B}T}} - 1}\ .$$

Because one mole contains $3\,N_\mathrm{A}$ oscillators the molar heat capacity is given by

$$C_V = 3\,N_\mathrm{A}\left(\frac{\partial\bar{E}}{\partial T}\right)_V = 3\,R \cdot \frac{\mathrm{e}^{\frac{\hbar\omega}{k_\mathrm{B}T}}}{\left(\mathrm{e}^{\frac{\hbar\omega}{k_\mathrm{B}T}} - 1\right)^2}\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right)^2\ .$$

Einstein's theory postulates one frequency $\omega = \omega_\mathrm{E}$ for all oscillators. Using the Boltzmann relation it is possible to assign a characteristic temperature

$$\theta_\mathrm{E} = \frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}}$$

such that

$$C_V = 3\,R \cdot \frac{\mathrm{e}^{\frac{\theta_\mathrm{E}}{T}}}{\left(\mathrm{e}^{\frac{\theta_\mathrm{E}}{T}} - 1\right)^2}\left(\frac{\theta_\mathrm{E}}{T}\right)^2\ .$$

This result of Einstein's theory describes the temperature dependence of the heat capacity in a qualitatively correct way. In the high temperature limit C_V tends to $3\,R$ as required by the equipartition law and in the low temperature limit C_V tends to zero. But from a quantitative point of view the description is still very bad: Experiments show that in the low temperature limit C_V is proportional to T^3 whereas Einstein's theory predicts an exponential dependence of temperature.

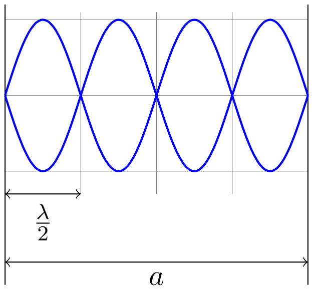

Figure 1: Standing wave

1.3. Debye's theory of the specific heat capacity

Einstein's theory makes the oversimplified assumption that all $3N_\mathrm{A}$ oscillators are independent of each other and oscillate with the same mean frequency ω_E. If a more general spectral frequency distribution is given by $z(\omega)\,\mathrm{d}\omega$, the internal energy U_M can be written as

$$U_\mathrm{M} = \int\limits_0^\infty \bar{E}(\omega, T) \cdot z(\omega)\,\mathrm{d}\omega$$

with $\bar{E}$ again the mean energy of one linear oscillator. Einstein's theory would describe the special case of a spectral frequency distribution given by the Dirac delta-function:

$$z_\mathrm{E}(\omega)\,\mathrm{d}\omega = 3\,N_\mathrm{A} \cdot \delta(\omega - \omega_\mathrm{E})\,\mathrm{d}\omega$$

Obviously, every improvement of his theory has to start by considering the interactions between the different oscillators and therefore by postulating a more realistic description of the distribution function $z(\omega)$.

The knowledge of part of the lattice spectrum is the starting point for Debye's theory. If the wavelength is large compared to the distance of the lattice points we have elastic waves with a propagation speed that is wavelength independent. First we consider the one-dimensional case of a standing wave between two parallel walls with distance a with the relation (see figure 1)

$$a = n_1 \cdot \frac{\lambda}{2}\,.$$

The number n_ol of modes with wavelength larger than a given λ_min is therefore

$$n_\mathrm{ol} = \frac{a}{\frac{1}{2}\lambda_\mathrm{min}}\,,$$

i.e. the distance a measured in units of $\frac{1}{2}\,\lambda_\mathrm{min}$. If we assume an isotropic medium it is easy to generalize this to the three-dimensional case: Considering only positive n, the

number of modes with wavelength larger than λ_{min} is given by the volume of an octant with radius a measured in volume units of $\left(\frac{1}{2}\,\lambda_{\text{min}}\right)^3$. This result has to be multiplied with 3 because a given wave vector $\vec{k}$ is related to one longitudinal and two transversal oscillations.
Therefore

$$n = 3 \cdot \frac{1}{8} \cdot \frac{4\pi}{3} a^3 \cdot \frac{1}{\left(\frac{1}{2}\,\lambda_{\text{min}}\right)^3} \ .$$

The number of modes per cubic centimeter follows if $a = 1$ cm:

$$n = \frac{3}{8} \cdot \frac{4\pi}{3} \cdot \frac{1}{\left(\frac{1}{2}\,\lambda_{\text{min}}\right)^3} \ .$$

With the molar volume V

$$n_{\text{mol}} = \frac{3}{8} \cdot \frac{4\pi}{3} \cdot \frac{V}{\left(\frac{1}{2}\,\lambda_{\text{min}}\right)^3} \ .$$

The relation $\lambda_{\text{min}} = 2\pi \cdot \frac{c}{\omega}$ allows us to express this in terms of frequency:

$$n_{\text{mol}} = \frac{3}{8} \cdot \frac{4\pi}{3} \cdot \frac{V}{\left(\pi \frac{c}{\omega}\right)^3} = \frac{1}{2} \cdot \frac{V}{\pi^2 c^3} \omega^3 \ ,$$

where c is the speed of sound.
(More precisely, we should write ω_{max} because ω is the frequency corresponding to the minimal wavelength λ_{min}. For simplicity we drop the label "max" in the following.)
From this we find the spectral frequency distribution

$$z(\omega)\,\mathrm{d}\omega = \frac{\partial n_{\text{mol}}}{\partial \omega}\,\mathrm{d}\omega = \frac{V}{2\pi^2} \cdot \frac{3}{c^3} \omega^2\,\mathrm{d}\omega \ .$$

All these results can be easily applied to the anisotropic case by replacing c with a more general speed of sound $\bar{c}$. Because every wave vector $\vec{k}$ relates to one longitudinal and two transversal oscillations, the general speed of sound can be defined by

$$\frac{3}{\bar{c}^3} = \frac{1}{c_{\text{l}}^3} + \frac{2}{c_{\text{tr}}^3}$$

with the longitudinal speed of sound c_{l} and the transversal speed of sound c_{tr}.
Debye extrapolated the elastic spectrum to higher frequencies in order to fit the total number of modes to exactly $3\,N_{\text{A}}$:

$$\int\limits_0^{\omega_{\text{D}}} z(\omega)\,\mathrm{d}\omega = n_{\text{mol}}(\omega_{\text{D}}) = \frac{V}{2} \cdot \frac{\omega_{\text{D}}^3}{\pi^2 \bar{c}^3} = 3\,N_{\text{A}}$$

$$\Rightarrow \omega_{\mathrm{D}} = \left(6\, N_{\mathrm{A}} \pi^2 \bar{c}^3 \cdot \frac{1}{V}\right)^{\frac{1}{3}}$$

So in Debye's theory

$$z(\omega) = \begin{cases} \frac{3\,V}{2\pi^2 \bar{c}^3}\omega^2 = 3\,N_{\mathrm{A}} \cdot \frac{3\,\omega^2}{\omega_{\mathrm{D}}^3} & \text{for } 0 \le \omega \le \omega_{\mathrm{D}} \\ 0 & \text{for } \omega > \omega_{\mathrm{D}} \end{cases} \tag{1}$$

Therefore

$$U_{\mathrm{M}} = \int\limits_0^{\omega_{\mathrm{D}}} \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\mathrm{e}^{\frac{\hbar\omega}{k_{\mathrm{B}}T}} - 1}\right] 3\,N_{\mathrm{A}} \cdot \frac{3\,\omega^2}{\omega_{\mathrm{D}}^3}\,\mathrm{d}\omega$$

and for the molar heat capacity

$$C_V = 3\,N_{\mathrm{A}} k_{\mathrm{B}} \int\limits_0^{\omega_{\mathrm{D}}} \frac{\mathrm{e}^{\frac{\hbar\omega}{k_{\mathrm{B}}T}}}{\left(\mathrm{e}^{\frac{\hbar\omega}{k_{\mathrm{B}}T}} - 1\right)^2} \cdot \left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2 \cdot \frac{3\,\omega^2}{\omega_{\mathrm{D}}^3}\,\mathrm{d}\omega\ .$$

Defining the *Debye temperature* θ as

$$\theta = \frac{\hbar\omega_{\mathrm{D}}}{k_{\mathrm{B}}}\ ,$$

the above expression can be simplified to

$$C_V\left(\frac{\theta}{T}\right) = 3\,R \cdot 3\left(\frac{T}{\theta}\right)^3 \int\limits_0^{\frac{\theta}{T}} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x = 3\,R \cdot D\left(\frac{\theta}{T}\right)$$

with $x = \frac{\hbar\omega}{k_{\mathrm{B}}T}$. The function $D\left(\frac{\theta}{T}\right)$ defined by this equation is called *Debye function* (see figure 2).
A totally equivalent expression for the Debye function is given by

$$D\left(\frac{\theta}{T}\right) = 12\left(\frac{T}{\theta}\right)^3 \int\limits_0^{\frac{\theta}{T}} \frac{x^3\,\mathrm{d}x}{\mathrm{e}^x - 1} - 3\left(\frac{\theta}{T}\right) \cdot \frac{1}{\mathrm{e}^{\frac{\theta}{T}} - 1}\ . \tag{2}$$

The Debye function (the integral in equation (2) is not analytically solvable) however can be calculated numerically (for example with the *quad()* function in Matlab).

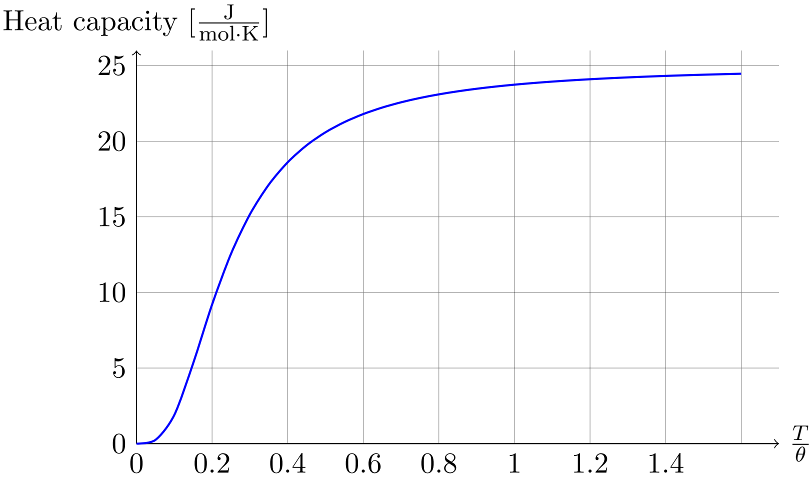

Figure 2: Debye function of Byrillium

Limit cases

- High temperature limit: $\frac{\theta}{T} \ll 1$
  By Taylor expanding $C_V\left(\frac{\theta}{T}\right)$ we find basically the law of Dulong-Petit:
  $$C_V = 3\,R\left[1 - \frac{1}{20}\left(\frac{\theta}{T}\right)^2 + \cdots\right]$$
- For low temperatures the integral can be expanded to ∞ and takes a constant value:
  $$C_V = \frac{12\,\pi^4}{5}R \cdot \left(\frac{T}{\theta}\right)^3 = 1943.8\,\frac{\mathrm{J}}{\mathrm{mol \cdot K}} \cdot \left(\frac{T}{\theta}\right)^3$$

The temperature dependence of the heat capacity is determined only by a temperature θ that is characteristic for each material. This theory agrees very well with experimental results; the curves can be best matched if one allows for a weak temperature dependence $\theta_{(T)}$.

1.4. Born's approach

Every attempt to calculate the experimental curves more precisely needs a more complex model for the spectral distribution $z(\omega)$.
In the simplified theories treated so far we always worked with a mean speed of sound $\bar{c}$. It is however possible to split this in a longitudinal and a transversal part. Requiring that both modes have a common minimal wavelength we arrive at *Born's approach*:

$$\lambda_{\text{min}} = 2\pi \cdot \frac{c_{\text{l}}}{\omega_{\text{D,l}}} = 2\pi \cdot \frac{c_{\text{tr}}}{\omega_{\text{D,tr}}}$$

The corresponding spectral frequency distributions can be found by inserting the defining equation for $\bar{c}$ in the expression for $z(\omega)$ (c.f. equation (1)):

$$z(\omega) = z_{\mathrm{l}}(\omega) + z_{\mathrm{tr}}(\omega) = \frac{V}{2\pi^2}\left[\frac{1}{c_{\mathrm{l}}^3} + \frac{2}{c_{\mathrm{tr}}^3}\right]\omega^2\,\mathrm{d}\omega = N_{\mathrm{A}}\cdot\frac{3\,\omega^2}{\omega_{\mathrm{D,l}}^3} + 2\,N_{\mathrm{A}}\cdot\frac{3\,\omega^2}{\omega_{\mathrm{D,tr}}^3} \tag{3}$$

Now we postulate two different cut-off frequencies $\omega_{\mathrm{D,l}}$ and $\omega_{\mathrm{D,tr}}$ for $z_{\mathrm{l}}(\omega)$ and $z_{\mathrm{tr}}(\omega)$ respectively, defined by:

$$\int_0^{\omega_{\mathrm{D,l}}} z_{\mathrm{l}}(\omega)\,\mathrm{d}\omega = N_{\mathrm{A}} \qquad \text{and} \qquad \int_0^{\omega_{\mathrm{D,tr}}} z_{\mathrm{tr}}(\omega)\,\mathrm{d}\omega = 2\,N_{\mathrm{A}}$$

Thus both the condition that the sum of all modes has to be exactly $3\,N_{\mathrm{A}}$ and Born's approach are satisfied and we continue analogously to the simplified theory and find

$$C_{V,\mathrm{Born}}\left(\frac{\theta_{\mathrm{l}}}{T}, \frac{\theta_{\mathrm{tr}}}{T}\right) = R\left[D\left(\frac{\theta_{\mathrm{l}}}{T}\right) + 2\,D\left(\frac{\theta_{\mathrm{tr}}}{T}\right)\right]$$

by introducing two new Debye temperatures

$$\theta_{\mathrm{l}} = \frac{\hbar\omega_{\mathrm{D,l}}}{k_{\mathrm{B}}} \qquad \text{and} \qquad \theta_{\mathrm{tr}} = \frac{\hbar\omega_{\mathrm{D,tr}}}{k_{\mathrm{B}}}\ .$$

Because the speed of sound is proportional to ω and thus also to the Debye temperature, we can define a mean Debye temperature θ in the same way we defined a mean speed of sound:

$$\frac{3}{\theta^3} = \frac{1}{\theta_{\mathrm{l}}^3} + \frac{2}{\theta_{\mathrm{tr}}^3}\ .$$

The simplified theory operates with exactly this mean Debye temperature.

For reasons not being discussed here the approximation made by Born's approach is in most cases not more precise than the simple model $C_V\left(\frac{\theta}{T}\right)$ even though the complex model is much closer to reality.

For comparison we plot the two spectral distributions (see figure 3). The following equations are convenient for the calculations (c.f. equations (1) and (3)):

$$\begin{aligned}
z(\omega)_{\mathrm{Debye}} &= 3\,N_{\mathrm{A}}\cdot\frac{3\,\omega^2}{\omega_{\mathrm{D}}^3} = \frac{3\,N_{\mathrm{A}}}{\omega_{\mathrm{D}}}\cdot 3\left(\frac{\omega}{\omega_{\mathrm{D}}}\right)^2 \\
z(\omega)_{\mathrm{Born}} &= z_{\mathrm{l}}(\omega) + z_{\mathrm{tr}}(\omega) = 3\,N_{\mathrm{A}}\left[\frac{\omega^2}{\omega_{\mathrm{D,l}}^3} + \frac{2\,\omega^2}{\omega_{\mathrm{D,tr}}^3}\right] \\
&= \frac{3\,N_{\mathrm{A}}}{\omega_{\mathrm{D}}}\left[\left(\frac{\omega_{\mathrm{D}}}{\omega_{\mathrm{D,l}}}\right)^3\left(\frac{\omega}{\omega_{\mathrm{D}}}\right)^2 + 2\left(\frac{\omega_{\mathrm{D}}}{\omega_{\mathrm{D,tr}}}\right)^3\left(\frac{\omega}{\omega_{\mathrm{D}}}\right)^2\right]
\end{aligned}$$

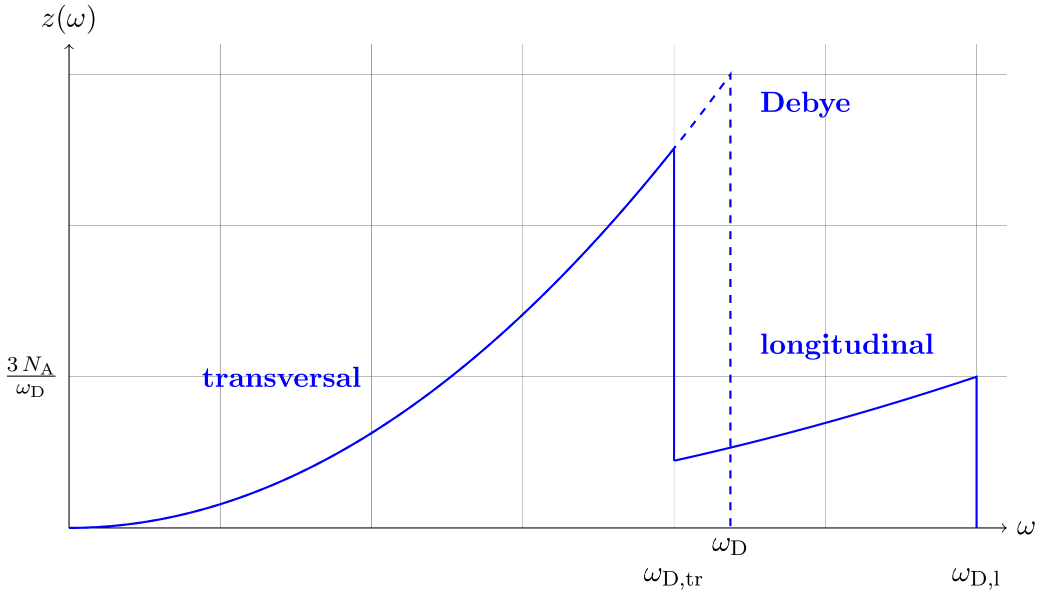

Figure 3: Frequency distributions from Debye's and Born's theories

1.5. Relation between the Debye temperature and the elastic properties of bodies in the solid state

From $\theta = \frac{\hbar}{k_B} \cdot \omega_D$ with

$$\omega_D = \left[6\,N_A \pi^2 \bar{c}^3 \cdot \frac{1}{V}\right]^{\frac{1}{3}} \qquad \text{and} \qquad V = \frac{M}{\varrho}$$

where V is the molar volume, M is the molar mass and ϱ is the density, we find the following relation between θ and $\bar{c}$:

$$\theta = \frac{\hbar}{k_B} \cdot \left[6\,N_A \pi^2 \cdot \frac{\varrho}{M}\right]^{\frac{1}{3}} \bar{c}$$

As stated in [4] the longitudinal and transversal speed of sound in isotropic bodies are given by

$$c_l = \left[\frac{E}{\varrho} \cdot \frac{1-u}{1-u-2u^2}\right]^{\frac{1}{2}} \qquad c_{tr} = \left[\frac{E}{\varrho} \cdot \frac{1}{2(1+u)}\right]^{\frac{1}{2}} ,$$

where E denotes Young's modulus and ϱ Poisson's ratio.
Inserting these expressions in

$$\frac{3}{\bar{c}^3} = \frac{1}{c_l^3} + \frac{2}{c_{tr}^3}$$

we arrive at

$$\theta = \frac{\hbar}{k_\mathrm{B}} \cdot \left[18\pi^2 \cdot \frac{N_\mathrm{A}\varrho}{M} \cdot \left(\frac{E}{\varrho}\right)^{\frac{3}{2}} \cdot \frac{1}{17 \cdot \left(\frac{2}{3}\right)^{\frac{3}{2}}} \right]^{\frac{1}{3}} .$$

Where we have used the approximation $u \approx \frac{1}{3}$ that is usually fulfilled very good for metals.
With $E = 31500 \, \frac{\mathrm{kp}}{\mathrm{mm}^2}$ (from [4]) for beryllium we find

$$\theta = 1320 \text{ K} .$$

This calculated value agrees well with other values in literature: By [3] the Debye temperature of beryllium is

$$\theta = 1160 \text{ K} .$$

1.6. Heat capacity of free electrons

So far we have only considered the heat capacity of lattice atoms. If there are additional free electrons they also contribute to the heat capacity. Free electrons are treated as a gas not influenced by the lattice. The classical treatment of this electron gas using kinetic gas theory states that every free electron contributes with

$$u_\mathrm{e} = \frac{3}{2} k_\mathrm{B} T$$

to the internal energy and with $\frac{3}{2\,k_\mathrm{B}}$ to the heat capacity.
For metals we make the assumption that there is one free electron per atom, so that these electrons increase the heat capacity by about $\frac{3}{2}R$, e.g. we expect for the molar heat capacity of a metal

$$C_V = C_{V \text{ (lattice)}} + C_{V \text{ (free electrons)}} = 3\,R + \frac{3\,R}{2} = \frac{9\,R}{2}$$

But experiments in the high temperature limit give results predicted by the law of Dulong-Petit with $C_V = 3\,R$, i.e. the heat capacity of the elecron gas should vanish in first approximation. The free electron gas does not behave like an ideal gas and thus cannot be described with Maxwell-Boltzmann statistics.
The electron gas consists of elementary particles with half-integral spin. Therefore, it has to be described by the Fermi distribution based on Pauli's principle in a quantum mechanical calculation. In the case of very diluted gases the Fermi distribution approaches the Boltzmann distribution. In this scenario the *density of the electron gas is so high* that we cannot use the approximation of Boltzmann statistics. This is the reason for the wrong result of the classical calculation. By using Fermi statistics and by treating the electron gas as a degenerate Fermi gas we find the correct result for the heat capacity of

the gas that vanishes at first approximation. In the second approximation we find – by Taylor expanding C_V (the integrals cannot be analytically solved) – the expression for the *low temperature limit*:

$$C_{V\ \text{(free electrons)}} = \gamma \cdot T \qquad \text{with } \gamma = \pi^2 \cdot \left(\frac{M}{\varrho}\right)^{\frac{2}{3}} \cdot (zN_\text{A})^{\frac{1}{3}} \cdot \frac{k_\text{B}^2 \cdot m_\text{e}}{(3\pi^2)^{\frac{2}{3}} \cdot \hbar^2}\ ,$$

where z is the number of conduction electrons per atom and M is the molar mass.
For Beryllium $\gamma = 4.92 \cdot 10^{-4}\,\frac{\text{J}}{\text{mol}\cdot\text{K}^2}$ (using $z = 2$).
On the other hand we know that for low temperatures (assuming $\theta = 1000$ K)

$$C_{V\ \text{(lattice)}} = 1943.8 \cdot 10^{-9}\,\frac{\text{J}}{\text{mol}\cdot\text{K}^4} \cdot T^3\ .$$

The temperature with equal contribution from the lattice and from the electron gas is therefore approximately at 15.9 K for beryllium.

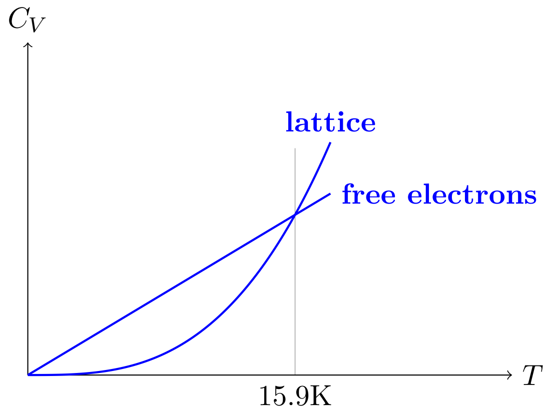

Figure 4: Lattice and electron gas contributions to the heat capacity

1.7. C_p–C_V correction

From the experiment we get values for the distribution of $C_p(T)$ whereas theories usually predict the function $C_V(T)$. In order to compare experimental results with theoretical predictions we need to find a mathematical relation between $C_p(T)$ and $C_V(T)$.
At constant pressure a temperature change ΔT changes the volume of a body by

$$\Delta V_\text{th} = 3\,\alpha \cdot V \cdot \Delta T$$

where α is the linear expansion coefficient.
Thereby we put work ΔA into the system where

$$\Delta A = -p \cdot \Delta V_\text{th} = -p \cdot 3\,\alpha \cdot V \cdot \Delta T$$

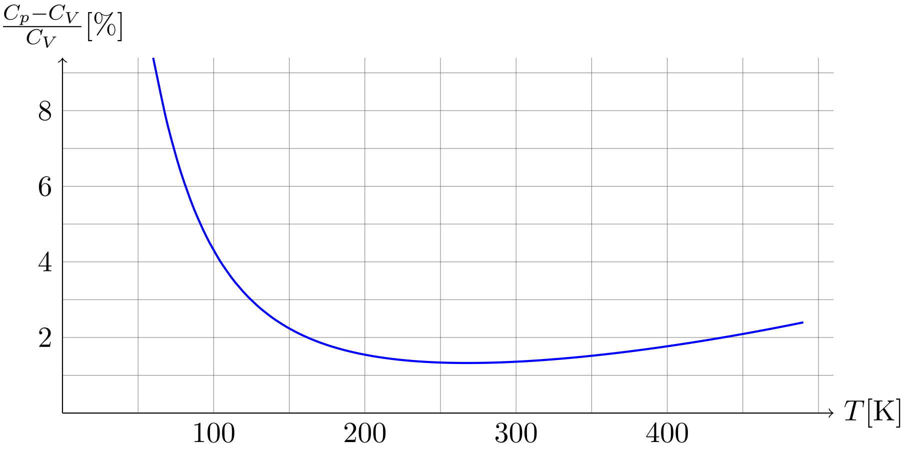

Figure 5: $C_p - C_V$-correction for beryllium

A change in pressure at constant temperature implies a change in volume given by the defining equation of the compressibility χ

$$\Delta V_{\mathrm{p}} = -\chi \cdot V \cdot \Delta p \; .$$

Because the volume should be constant we require

$$\Delta V_{\mathrm{th}} + \Delta V_{\mathrm{p}} = 0$$

and thus get a relation between Δp and ΔT:

$$\Delta p = \frac{3\,\alpha}{\chi} \cdot \Delta T$$

and

$$\begin{aligned}
(c_p - c_V)\,\Delta T &= -\Delta A \\
c_p - c_V &= -\frac{\Delta A}{\Delta T} = 3\,\alpha \cdot V \cdot p \\
\mathrm{d}\,(c_p - c_V) &= 3\,\alpha V \cdot \mathrm{d}p
\end{aligned}$$

Therefore,

$$\mathrm{d}\,(C_p - C_V) = 3\,\alpha v \cdot \frac{3\,\alpha}{\chi}\,\mathrm{d}T = \frac{9\,\alpha^2 v}{\chi}\,\mathrm{d}T$$

and by integration and replacing $v = \frac{M}{\varrho}$ (molar volume) we arrive at

$$C_p - C_V = \frac{9\,\alpha^2}{\chi} \cdot \frac{M}{\varrho} \cdot T \; .$$

Figure 5 shows the relative difference $\frac{C_p - C_V}{C_V}$ as a function of temperature without considering the temperature dependence of α, χ and ϱ.

1.8. The Debye temperature of beryllium

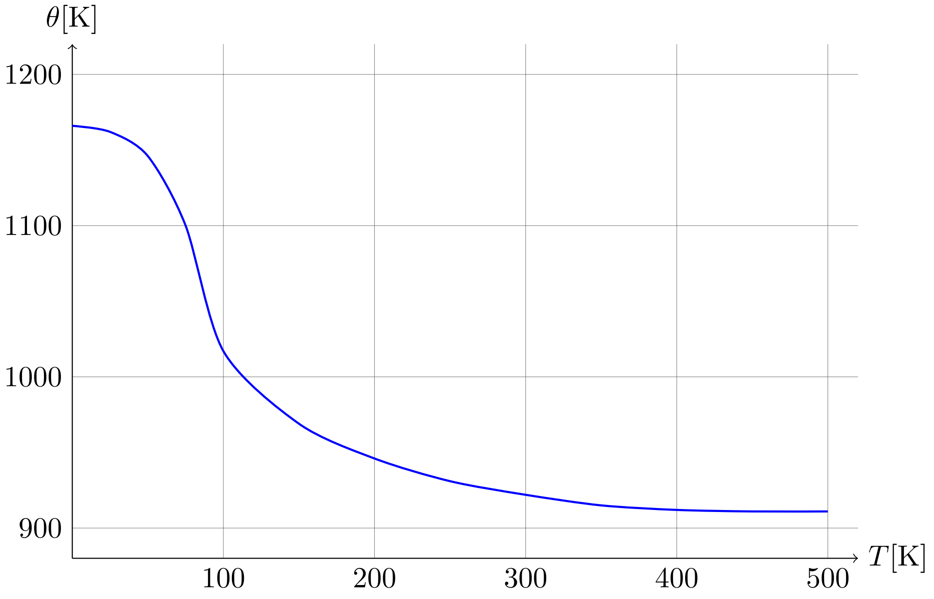

Figure 6: Debye temperature of beryllium

By deriving the Debye temperature we assumed a continuous body. Perturbations caused by the internal structure of matter are therefore not considered. If the specific heat capacity is examined over a large temperature interval it is clearly not possible to treat the Debye temperature as a constant value independent of T. The dependence of $C_V(T)$ for beryllium was measured in [7] and the temperature dependence of θ was calculated. Figure 6 shows the corresponding results.

This temperature dependency has to be considered in order to precisely calculate the curve of the specific heat capacity.

2. Equipment

2.1. Calorimeter

The experiment should provide the possibility to measure the specific heat capacity with only one calorimeter over a temperature interval as large as possible (see section 3.4). These requirements suggested to use a Nernst calorimeter that is based on the following two principles: The sample is heated up by electric energy and a vacuum isolation prevents heat exchange with the environment.

Because we want to take measurements over a large temperature interval we need to be able to heat up or cool down the sample to every given temperature between −180° C and +100° C. For low temperatures we cool the entire calorimeter with liquid nitrogen. An exchange gas in the space between the sample and the metal casing of the calorimeter

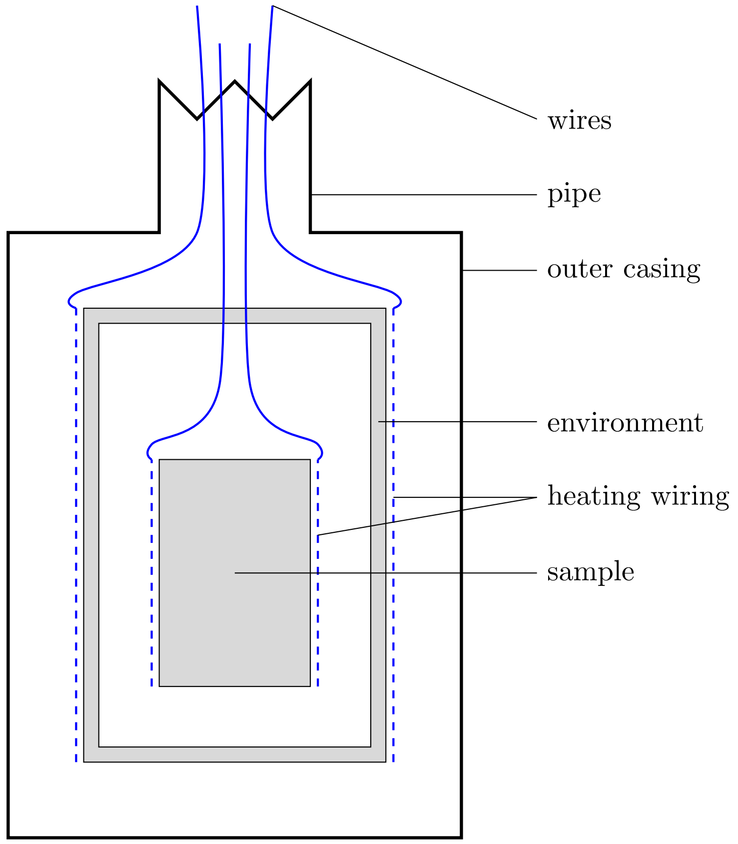

Figure 7: Diagram of the experimental setup

with good thermal conduction facilitates this process. During the measurements of the specific heat capacity the sample has to be isolated as well as possible. The heat lost by radiation and thermal conductance through the fixing wires can be neglected if the temperature difference between the sample and its immediate environment is small. But the outer metal casing has a fixed temperature (i.e. room temperature) whereas the sample temperature varies in a large interval. The resulting temperature differences would influence the measured values too much. Therefore, there is another copper casing in between the sample and the outer casing that can be heated up independently of the sample. This inner casing is simply called environment in the following. So it is possible to keep the temperature difference between the sample and the environment at a low level while the only large temperature difference occurs between the two layers of casings. With this method we can reduce the heat radiation to an absolute minimum. The temperatures of the sample and the environment are measured by thermocouple elements (T_s and T_e).

These considerations decided at large the design of the calorimeter. Engineering feasibility led to a cylindrical design with a concentric arrangement of the sample and the casings (see figure 7).

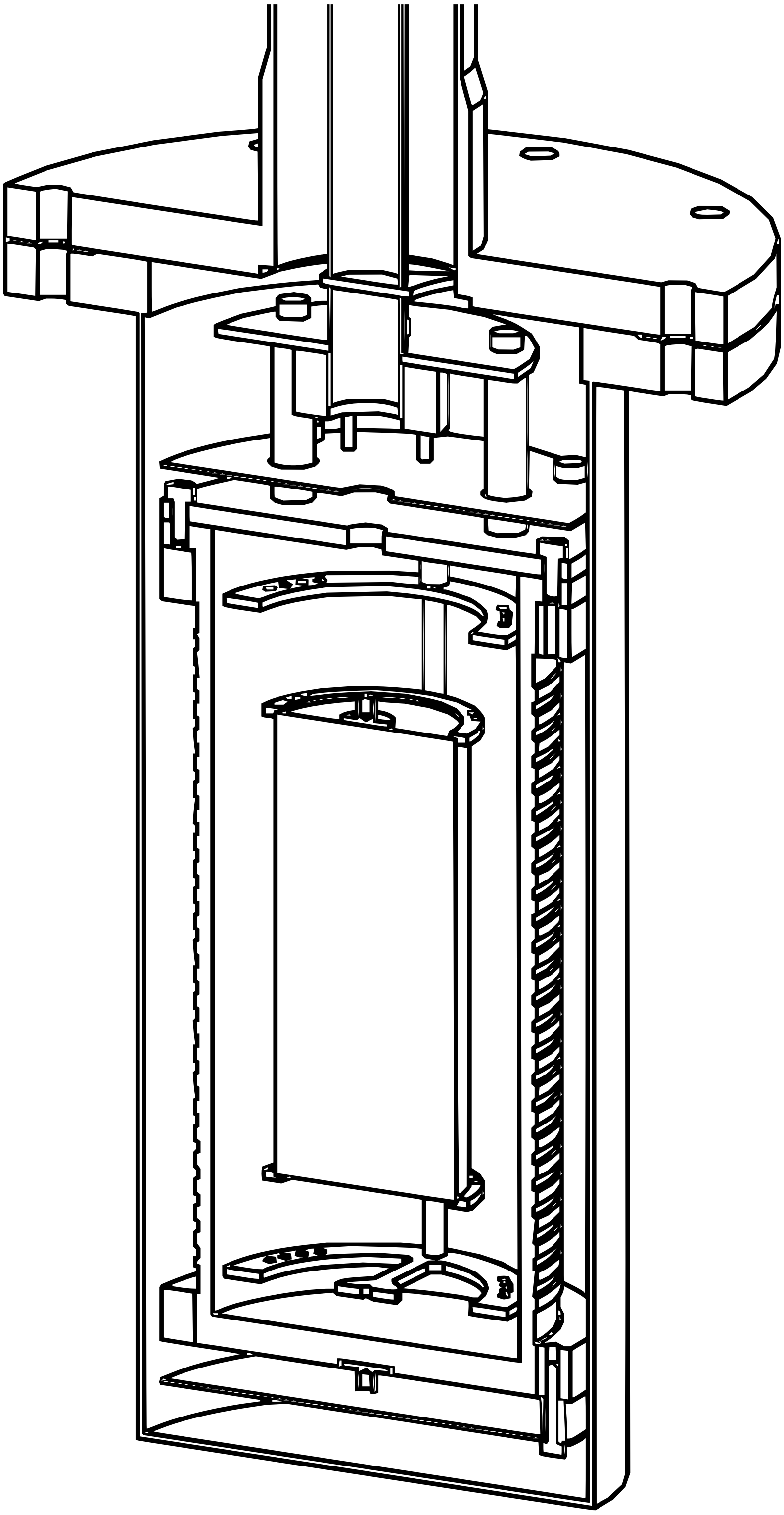

Figure 8: Exact drawing of the experimental setup

Much work went into constructing the calorimeter in a way that makes it possible to easily disassemble it into its building parts. On the other hand only building parts that can sustain the temperature variation from $-200°$ C to $+100°$ C could be used. To maintain a good vacuum over the whole range of temperatures it was necessary to avoid all substances with a high vapor pressure inside the calorimeter.

The outer metal casing is made of stainless steel with a sealing ring made of indium (rubber was not a possibility for the high vacuum needed). The gas pipe has to have a certain length such that the calorimeter can be lowered without cooling the other parts (e.g. the heating wires and the valves) too much. The pipe is also made of stainless steel because of its stability and its very low thermal conductance.

The beryllium sample has a mass of approximately 90 g and a purity grade of 98.8%. The sample is covered by a layer of teflon (polytetrafluoroethylene) band providing a good insulation. It is attached to two teflon rings that are used as a suspension attachment. (Please consult the appendix for more precise numbers.) The environment (inner casing) is made of copper. Its temperature should be kept constant during the experiment and it should be very massive in order not to be susceptible to temperature fluctuations. Then again the total heat capacity of the calorimeter should be as small as possible so that it can be cooled down efficiently. Thus, the actual size of the copper environment is a trade-off between the two requirements. Again a thin layer of teflon band was used to insulate the wiring. For exact technical details see figure 8.

2.2. The vacuum pump

The calorimeter has two valves. One *venting valve* to the outside and one that is connected to the vacuum pump. To evacuate the calorimeter both valves are closed, the pump is started and then the connecting valve slowly opened.

2.3. Temperature measurements

Two copper-constantan (type T) or Chromel-Alumel (type K) thermocouple elements allow to measure the temperature of both the sample and the environment. As a reference point we use a pot with ice-water (it should always contain *a lot* of ice). For conversion of the measured values to temperatures please refer to the tables on page 21 till 24.

2.4. Heating

As mentioned above the sample and the environment can be heated up independently using electrical energy. For the exact wiring please refer to figure 9.

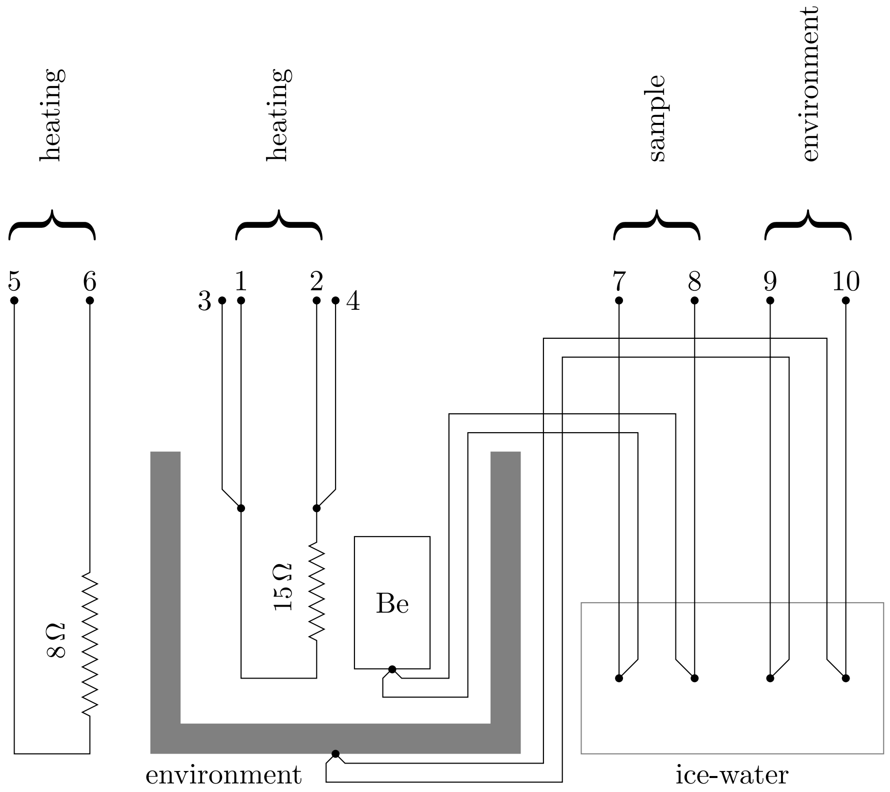

Figure 9: Wiring of the experiment (note: The resistance of the heating elements is temperature dependent)

thermo couple voltage as a function of temperature (Type T)

[E/mV] type T (Cu-CuNi)

Limits of error (whichever is greater): 1.0°C or 0.75% Above 0°C, 1.0°C or 1.5% Below 0°C

t90 [°C]	**.0**	**.1**	**.2**	**.3**	**.4**	**.5**	**.6**	**.7**	**.8**	**.9**	**t90** [°C]
-270	-6.258										**-270**
-260	-6.232	-6.236	-6.239	-6.242	-6.245	-6.248	-6.251	-6.253	-6.255	-6.256	**-260**
-250	-6.180	-6.187	-6.193	-6.198	-6.204	-6.209	-6.214	-6.219	-6.223	-6.228	**-250**
-240	-6.105	-6.114	-6.122	-6.130	-6.138	-6.146	-6.153	-6.160	-6.167	-6.174	**-240**
-230	-6.007	-6.017	-6.028	-6.038	-6.049	-6.059	-6.068	-6.078	-6.087	-6.096	**-230**
-220	-5.888	-5.901	-5.914	-5.925	-5.938	-5.950	-5.962	-5.973	-5.985	-5.996	**-220**
-210	-5.753	-5.767	-5.782	-5.795	-5.809	-5.823	-5.836	-5.850	-5.863	-5.876	**-210**
-200	-5.603	-5.619	-5.634	-5.650	-5.665	-5.688	-5.695	-5.710	-5.724	-5.739	**-200**
-190	-5.439	-5.456	-5.473	-5.489	-5.506	-5.523	-5.539	-5.555	-5.571	-5.587	**-190**
-180	-5.261	-5.279	-5.297	-5.316	-5.334	-5.351	-5.369	-5.387	-5.404	-5.421	**-180**
-170	-5.070	-5.089	-5.109	-5.128	-5.148	-5.167	-5.186	-5.205	-5.224	-5.242	**-170**
-160	-4.865	-4.886	-4.907	-4.928	-4.949	-4.969	-4.989	-5.010	-5.030	-5.050	**-160**
-150	-4.648	-4.671	-4.693	-4.715	-4.737	-4.759	-4.780	-4.802	-4.823	-4.844	**-150**
-140	-4.419	-4.443	-4.466	-4.489	-4.512	-4.535	-4.558	-4.581	-4.604	-4.626	**-140**
-130	-4.177	-4.202	-4.226	-4.251	-4.275	-4.300	-4.324	-4.348	-4.372	-4.395	**-130**
-120	-3.923	-3.949	-3.975	-4.000	-4.026	-4.052	-4.077	-4.102	-4.127	-4.152	**-120**
-110	-3.657	-3.684	-3.711	-3.738	-3.765	-3.791	-3.818	-3.844	-3.871	-3.897	**-110**
-100	-3.379	-3.407	-3.435	-3.463	-3.491	-3.519	-3.547	-3.574	-3.602	-3.629	**-100**
-90	-3.089	-3.118	-3.148	-3.177	-3.206	-3.235	-3.264	-3.293	-3.322	-3.350	**-90**
-80	-2.788	-2.818	-2.849	-2.879	-2.910	-2.940	-2.970	-3.000	-3.030	-3.059	**-80**
-70	-2.476	-2.507	-2.539	-2.571	-2.602	-2.633	-2.664	-2.695	-2.726	-2.757	**-70**
-60	-2.153	-2.186	-2.218	-2.251	-2.283	-2.316	-2.348	-2.380	-2.412	-2.444	**-60**
-50	-1.819	-1.853	-1.887	-1.920	-1.954	-1.987	-2.021	-2.054	-2.087	-2.120	**-50**
-40	-1.475	-1.510	-1.545	-1.579	-1.614	-1.648	-1.683	-1.717	-1.751	-1.785	**-40**
-30	-1.121	-1.157	-1.192	-1.228	-1.264	-1.299	-1.335	-1.370	-1.405	-1.440	**-30**
-20	-0.757	-0.794	-0.830	-0.867	-0.904	-0.940	-0.976	-1.013	-1.049	-1.085	**-20**
-10	-0.383	-0.421	-0.459	-0.496	-0.534	-0.571	-0.608	-0.646	-0.683	-0.720	**-10**
-0	0.000	-0.039	-0.077	-0.116	-0.154	-0.193	-0.231	-0.269	-0.307	-0.345	**-0**

thermo couple voltage as a function of temperature (Type T)

[E/mV] type T (Cu-CuNi)

Limits of error (whichever is greater): 1.0°C or 0.75% Above 0°C, 1.0°C or 1.5% Below 0°C

t90 [°C]	**.0**	**.1**	**.2**	**.3**	**.4**	**.5**	**.6**	**.7**	**.8**	**.9**	**t90** [°C]
0	0.000	0.039	0.078	0.117	0.156	0.195	0.234	0.273	0.312	0.352	**0**
10	0.391	0.431	0.470	0.510	0.549	0.589	0.629	0.669	0.709	0.749	**10**
20	0.790	0.830	0.870	0.911	0.951	0.992	1.033	1.074	1.114	1.155	**20**
30	1.196	1.238	1.279	1.320	1.362	1.403	1.445	1.486	1.528	1.570	**30**
40	1.612	1.654	1.696	1.738	1.780	1.823	1.865	1.908	1.950	1.993	**40**
50	2.036	2.079	2.122	2.165	2.208	2.251	2.294	2.338	2.381	2.425	**50**
60	2.468	2.512	2.556	2.600	2.643	2.687	2.732	2.776	2.820	2.864	**60**
70	2.909	2.953	2.998	3.043	3.087	3.132	3.177	3.222	3.267	3.312	**70**
80	3.358	3.403	3.448	3.494	3.539	3.585	3.631	3.677	3.722	3.768	**80**
90	3.814	3.860	3.907	3.953	3.999	4.046	4.092	4.138	4.185	4.232	**90**
100	4.279	4.325	4.372	4.419	4.466	4.513	4.561	4.608	4.655	4.702	**100**
110	4.750	4.798	4.845	4.893	4.941	4.988	5.036	5.084	5.132	5.180	**110**
120	5.228	5.277	5.325	5.373	5.422	5.470	5.519	5.567	5.616	5.665	**120**
130	5.714	5.763	5.812	5.861	5.910	5.959	6.008	6.057	6.107	6.156	**130**
140	6.206	6.255	6.305	6.355	6.404	6.454	6.504	6.554	6.604	6.654	**140**
150	6.704	6.754	6.805	6.855	6.905	6.956	7.006	7.057	7.107	7.158	**150**
160	7.209	7.260	7.310	7.361	7.412	7.463	7.515	7.566	7.617	7.668	**160**
170	7.720	7.771	7.823	7.874	7.926	7.977	8.029	8.081	8.133	8.185	**170**
180	8.237	8.289	8.341	8.393	8.445	8.497	8.550	8.602	8.654	8.707	**180**
190	8.759	8.812	8.865	8.917	8.970	9.023	9.076	9.129	9.182	9.235	**190**
200	9.288	9.341	9.395	9.448	9.501	9.555	9.608	9.662	9.715	9.769	**200**
210	9.822	9.876	9.930	9.984	10.038	10.092	10.146	10.200	10.254	10.308	**210**
220	10.362	10.417	10.471	10.525	10.580	10.634	10.689	10.743	10.798	10.853	**220**
230	10.907	10.962	11.017	11.072	11.127	11.182	11.237	11.292	11.347	11.403	**230**
240	11.458	11.513	11.569	11.624	11.680	11.735	11.791	11.846	11.902	11.958	**240**

thermo couple voltage as a function of temperature (Type K)

[E/mV] type K (NiCr-NiMnAlSi)

Limits of error (whichever is greater): 2.2°C or 0.75% Above 0°C, 2.2°C or 2.0% Below 0°C

t90 [°C]	**.0**	**.1**	**.2**	**.3**	**.4**	**.5**	**.6**	**.7**	**.8**	**.9**	**t90** [°C]
-270	-6.458										**-270**
-260	-6.441	-6.444	-6.446	-6.448	-6.450	-6.452	-6.453	-6.455	-6.456	-6.457	**-260**
-250	-6.404	-6.408	-6.413	-6.417	-6.421	-6.425	-6.429	-6.432	-6.435	-6.438	**-250**
-240	-6.344	-6.351	-6.358	-6.364	-6.370	-6.377	-6.382	-6.388	-6.393	-6.399	**-240**
-230	-6.262	-6.271	-6.280	-6.289	-6.297	-6.306	-6.314	-6.322	-6.329	-6.337	**-230**
-220	-6.158	-6.170	-6.181	-6.192	-6.202	-6.213	-6.223	-6.233	-6.243	-6.252	**-220**
-210	-6.035	-6.048	-6.061	-6.074	-6.087	-6.099	-6.111	-6.123	-6.135	-6.147	**-210**
-200	-5.891	-5.907	-5.922	-5.936	-5.951	-5.965	-5.980	-5.994	-6.007	-6.021	**-200**
-190	-5.730	-5.747	-5.763	-5.780	-5.797	-5.813	-5.829	-5.845	-5.861	-5.876	**-190**
-180	-5.550	-5.569	-5.588	-5.606	-5.624	-5.642	-5.660	-5.678	-5.695	-5.713	**-180**
-170	-5.354	-5.374	-5.395	-5.415	-5.435	-5.454	-5.474	-5.493	-5.512	-5.531	**-170**
-160	-5.141	-5.163	-5.185	-5.207	-5.228	-5.250	-5.271	-5.292	-5.313	-5.333	**-160**
-150	-4.913	-4.936	-4.960	-4.983	-5.006	-5.029	-5.052	-5.074	-5.097	-5.119	**-150**
-140	-4.669	-4.694	-4.719	-4.744	-4.768	-4.793	-4.817	-4.841	-4.865	-4.889	**-140**
-130	-4.411	-4.437	-4.463	-4.490	-4.516	-4.542	-4.567	-4.593	-4.618	-4.644	**-130**
-120	-4.138	-4.166	-4.194	-4.221	-4.249	-4.276	-4.303	-4.330	-4.357	-4.384	**-120**
-110	-3.852	-3.882	-3.911	-3.939	-3.968	-3.997	-4.025	-4.054	-4.082	-4.110	**-110**
-100	-3.554	-3.584	-3.614	-3.645	-3.675	-3.705	-3.734	-3.764	-3.794	-3.823	**-100**
-90	-3.243	-3.274	-3.306	-3.337	-3.368	-3.400	-3.431	-3.462	-3.492	-3.523	**-90**
-80	-2.920	-2.953	-2.986	-3.018	-3.050	-3.083	-3.115	-3.147	-3.179	-3.211	**-80**
-70	-2.587	-2.620	-2.654	-2.688	-2.721	-2.755	-2.788	-2.821	-2.854	-2.887	**-70**
-60	-2.243	-2.278	-2.312	-2.347	-2.382	-2.416	-2.450	-2.485	-2.519	-2.553	**-60**
-50	-1.889	-1.925	-1.961	-1.996	-2.032	-2.067	-2.103	-2.138	-2.173	-2.208	**-50**
-40	-1.527	-1.564	-1.600	-1.637	-1.673	-1.709	-1.745	-1.782	-1.818	-1.854	**-40**
-30	-1.156	-1.194	-1.231	-1.268	-1.305	-1.343	-1.380	-1.417	-1.453	-1.490	**-30**
-20	-0.778	-0.816	-0.854	-0.892	-0.930	-0.968	-1.006	-1.043	-1.081	-1.119	**-20**
-10	-0.392	-0.431	-0.470	-0.508	-0.547	-0.586	-0.624	-0.663	-0.701	-0.739	**-10**
0	0.000	-0.039	-0.079	-0.118	-0.157	-0.197	-0.236	-0.275	-0.314	-0.353	**0**

thermo couple voltage as a function of temperature (Type K)

[E/mV] type K (NiCr-NiMnAlSi)

Limits of error (whichever is greater): 2.2°C or 0.75% Above 0°C, 2.2°C or 2.0% Below 0°C

t90 [°C]	**.0**	**.1**	**.2**	**.3**	**.4**	**.5**	**.6**	**.7**	**.8**	**.9**	**t90** [°C]
0	0.000	0.039	0.079	0.119	0.158	0.198	0.238	0.277	0.317	0.357	**0**
10	0.397	0.437	0.477	0.517	0.557	0.597	0.637	0.677	0.718	0.758	**10**
20	0.798	0.838	0.879	0.919	0.960	1.000	1.041	1.081	1.122	1.163	**20**
30	1.203	1.244	1.285	1.326	1.366	1.407	1.448	1.489	1.530	1.571	**30**
40	1.612	1.653	1.694	1.735	1.776	1.817	1.858	1.899	1.941	1.982	**40**
50	2.023	2.064	2.106	2.147	2.188	2.230	2.271	2.312	2.354	2.395	**50**
60	2.436	2.478	2.519	2.561	2.602	2.644	2.685	2.727	2.768	2.810	**60**
70	2.851	2.893	2.934	2.976	3.017	3.059	3.100	3.142	3.184	3.225	**70**
80	3.267	3.308	3.350	3.391	3.433	3.474	3.516	3.557	3.599	3.640	**80**
90	3.682	3.723	3.765	3.806	3.848	3.889	3.931	3.972	4.013	4.055	**90**
100	4.096	4.138	4.179	4.220	4.262	4.303	4.344	4.385	4.427	4.468	**100**
110	4.509	4.550	4.591	4.633	4.674	4.715	4.756	4.797	4.838	4.879	**110**
120	4.920	4.961	5.002	5.043	5.084	5.124	5.165	5.206	5.247	5.288	**120**
130	5.328	5.369	5.410	5.450	5.491	5.532	5.572	5.613	5.653	5.694	**130**
140	5.735	5.775	5.815	5.856	5.896	5.937	5.977	6.017	6.058	6.098	**140**
150	6.138	6.179	6.219	6.259	6.299	6.339	6.380	6.420	6.460	6.500	**150**
160	6.540	6.580	6.620	6.660	6.701	6.741	6.781	6.821	6.861	6.901	**160**
170	6.941	6.981	7.021	7.060	7.100	7.140	7.180	7.220	7.260	7.300	**170**
180	7.340	7.380	7.420	7.460	7.500	7.540	7.579	7.619	7.659	7.699	**180**
190	7.739	7.779	7.819	7.859	7.899	7.939	7.979	8.019	8.059	8.099	**190**
200	8.138	8.178	8.218	8.258	8.298	8.338	8.378	8.418	8.458	8.499	**200**
210	8.539	8.579	8.619	8.659	8.699	8.739	8.779	8.819	8.860	8.900	**210**
220	8.940	8.980	9.020	9.061	9.101	9.141	9.181	9.222	9.262	9.302	**220**
230	9.343	9.383	9.423	9.464	9.504	9.545	9.585	9.626	9.666	9.707	**230**
240	9.747	9.788	9.828	9.869	9.909	9.950	9.991	10.031	10.072	10.113	**240**

3. Measurements

3.1. Introduction

The measurements of the specific heat capacity are based on the following idea: The sample is heated up by the use of electrical energy. The input energy

$$A_{\text{el (Joule)}} = VI \cdot t_{\text{h}}$$

is well known if the heating voltage V, the heating current I and the heating time t_{h} are measured.
The sample is heated up by an amount ΔT and absorbs the energy

$$A_{\text{th (Joule)}} = mc_p \cdot \Delta T \ .$$

where c_p is given in $\frac{\text{J}}{\text{g}\cdot\text{K}}$.
Neglecting heat losses we have

$$A_{\text{el}} = A_{\text{th}}$$

Because we know m and can measure ΔT it is easy to calculate c_p.
But in the experiment we always have $A_{\text{el}} > A_{\text{th}}$, i.e. it is never possible to use all input energy to heat up the sample:

1. The sample constantly loses heat:

   $$A_{\text{el}} = A_{\text{th}} + A_{\text{ lost}}$$

   The calculation of $A_{\text{th}} = A_{\text{el}} - A_{\text{ lost}}$ is described in detail in section 3.2.

2. Together with the sample other parts of the setup are heated up (e.g. the teflon, the wires, etc.) those additional heat capacities are interpreted as an increased heat capacity of the sample:

   $$A_{\text{th}} = A_{\text{th (sample)}} + A_{\text{th (other)}}$$

   For a detailed calculations see section 3.3.

Now we can calculate c_p from

$$A_{\text{th (sample)}} = mc_p \cdot \Delta T \cdot J \ .$$

3.2. Heat exchange with the environment

The main reasons for loss of heat to the environment are

1. heat conduction and convection of the surrounding air
2. heat conduction in the electrical wires
3. thermal radiation

The vacuum pump is able to reduce the pressure to a low value around the order of magnitude of 10^{-3} mbar. Together with the use of thin wires out of a material with low heat conductivity the heat conduction is reduced to a minimum. All three effects heavily depend on the temperature difference between the sample and its environment. Especially the heat radiation that scales with T^4, where T is the temperature difference, according to Stefan-Boltzmann's law.

The error due to the loss of heat can be compensated by answering the following question: How large would the initial increase in temperature ΔT_x have been if there was no heat exchange with the environment?

In the experiment it is possible to determine ΔT by measuring the temperature T_s of the sample before and after the actual heating. If we had a perfect thermal insulation the time dependence of the temperature would look like this:

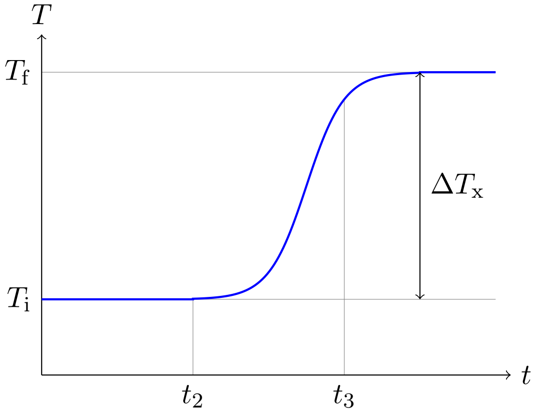

Figure 10: Ideal temperature evolution when heating the sample

In the beginning of the experiment the sample has a constant temperature T_i. During the time interval t_2 to t_3 the sample is heated up and after switching off the heating current it has a given final temperature T_f that remains constant. In this case ΔT_x is trivially given by

$$\Delta T_\mathrm{x} = T_\mathrm{f} - T_\mathrm{i}$$

In a real experiment however the curve looks more complex. We distinguish three phases: the initial period, the main period and the final period (see figure 11).

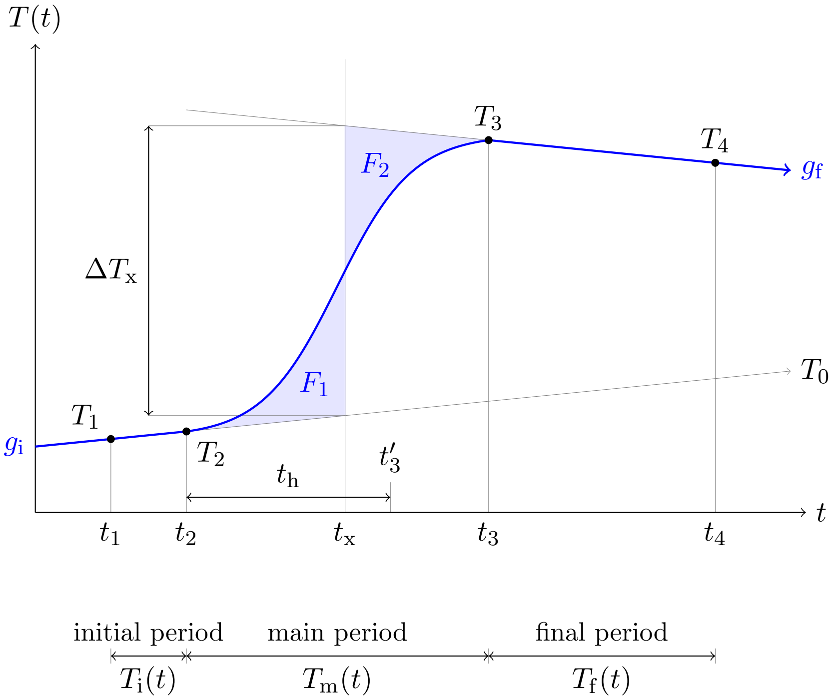

Figure 11: Characteristic temperature evolution when heating the sample

The experiment starts with the *initial period* ($T(t) = T_\mathrm{i}(t)$): If the temperature of the sample and the temperature of the environment T_0 differ the temperature of the sample changes until it reaches the value T_0. Once the difference gets small enough the function $T_\mathrm{i}(t)$ can be partially approximated by a straight line. The initial period should last until the value of $\frac{\partial T}{\partial t}$ remains roughly constant and hence it is possible to find the line g_i.

In the time interval between t_2 and t_3 the sample is heated up with electrical energy. The curve $T(t)$ in this segment shows a behavior that is determined by the heating power, the heat conduction of the sample, the heat exchange between the sample and the wires and by relaxation effects such as the response time of the thermocouple element.

The *main period* ($T(t) = T_\mathrm{m}(t)$) corresponds to the interval from t_2 to t_3 where t_3 is the time at which $T(t)$ takes the form of a line again.

At this point the *final period* ($T(t) = T_\mathrm{f}(t)$) starts. The measurements should be continued until the line g_f can be exactly determined.

The increase in temperature ΔT_x is completely determined by the amount of input energy. It cannot depend on the period of time t_h that was used to put the energy into the system. With decreasing t_h (but constant input energy) the slope gets steeper and steeper. The line would be vertical if the energy was put into the system in an infinitely short time interval (limit $t_\mathrm{h} \to 0$) and all relaxation times would vanish. Because there is no thermal exchange with the environment in an infinitely short time we could find

ΔT_x by just measuring the length of the vertical line segment.
Thus, our problem is reduced to the simple question: How do we have to chose t_x such that the limit case and the real process are energetically equivalent? We will realize that we have to take the value of t_x that equalizes the areas F_1 and F_2 (see figure 11).
Newton's *law of cooling* provides the theoretical explanation for this claim. It states that the temperature exchange between sample and environment per time unit is proportional to the temperature difference:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k\,(T_0 - T) \tag{4}$$

In the following we assume $T_2 < T_0 < T_3$ (see figure 11).
The straight line g_i is given by the function $T_\mathrm{i}(t)$. We now calculate the heat exchange between sample and environment in the time interval from t_2 to t_x by integrating equation (4):
For the idealized curve we find

$$Q_{1i} = k \int\limits_{t_2}^{t_\mathrm{x}} (T_0 - T_\mathrm{i}(t))\ \mathrm{d}t$$

and for the actual curve

$$Q_{1m} = k \int\limits_{t_2}^{t_x} (T_0 - T_\mathrm{m}(t))\ \mathrm{d}t\ .$$

If we follow the extrapolated curve $T_\mathrm{i}(t)$ instead of the real curve $T_\mathrm{m}(t)$ in the interval from t_2 to t_x we get an error

$$\Delta Q_1 = Q_{1i} - Q_{1m} = k \int\limits_{t_2}^{t_\mathrm{x}} (T_\mathrm{m}(t) - T_\mathrm{i}(t))\ \mathrm{d}t = k \cdot F_1\ .$$

And in an analog way we find the error

$$\begin{aligned}\Delta Q_2 &= Q_{2i} - Q_{2m} = k \int\limits_{t_\mathrm{x}}^{t_3} (T_0 - T_\mathrm{f}(t))\ \mathrm{d}t - k \int\limits_{t_\mathrm{x}}^{t_3} (T_0 - T_\mathrm{m}(t))\ \mathrm{d}t \\ &= -k \int\limits_{t_\mathrm{x}}^{t_3} (T_\mathrm{f} - T_\mathrm{m}(t))\ \mathrm{d}t = -k \cdot F_2\end{aligned}$$

in the interval from t_x to t_3.
And thus the total error

$$\Delta Q = \Delta Q_1 + \Delta Q_2 = k \cdot (F_1 - F_2)$$

vanishes if and only if $F_1 = F_2$.
The heat losses, i.e. the slopes of the lines g_i and g_f are smaller if the temperature difference between T and T_0 is smaller. Therefore, the best way to choose T_0 is to take the average value of T_2 and T_3. This is called “Rumford’s trick”.

3.3. Corrections to eliminate other heat capacities

Together with the beryllium sample also the teflon parts and the wires get heated up. Hence, the energy balance is given by

$$m_\mathrm{Be} \cdot c_\mathrm{Be} \cdot \Delta T + \sum_i m_i \cdot c_i \cdot \Delta T = A_\mathrm{th}$$

where the index i denotes to the teflon parts and the wires.
The specific heat capacity of teflon can be found in [8]. The table with the relevant values can also be found in the appendix on page 33.
The specific heat capacity of the wire (copper) can be calculated from the Debye function. The values $\theta = 343.5$ K, $\varrho = 8.94\,\frac{\mathrm{g}}{\mathrm{cm}^3}$, $M = 63.55\,\frac{\mathrm{g}}{\mathrm{mol}}$ are used.

3.4. Experimental procedure

The aim of this experiment is to determine $C_V(T)$ of beryllium over the temperature interval from $-196°$ C to $+100°$ C. (Consider why we use beryllium for this experiment.) Some hints related to the actual measurement can be found in the previous sections. The process is explained in detail and coherently in this section. In order to complete the experiment in a reasonable time it is very important to think of and write down a *measuring schedule*. It is recommended to use a main period of about 10 minutes and to chose about 5° C for ΔT_x. Before each measurement the heating energy should be estimated by using the Debye function.
First, a few measurements between room temperature and +100° C should be tried in order to get used to the setup with simple conditions.
To start the experiment both valves need to be closed and the vacuum pump started. The valve between the calorimeter and the pump should be slowly opened to evacuate the calorimeter. Now the specific heat capacity at room temperature can be determined as described above. Then the sample is heated up to the next temperature point one wants to measure and the measuring steps are repeated to get the new value of C_p. This process is continued step by step until the temperature +100° C is reached. Figure 12 pictorially describes this procedure. The air surrounding the calorimeter acts as a heating bath of about 20° C.
As soon as the measuring process is clear the whole interval from $-196°$ C to room temperature can be covered. The starting point is the lowest possible temperature (calorimeter fully lowered into liquid nitrogen).
We need an exchange gas in order to efficiently cool down the sample because the vacuum in the calorimeter would insulate it. We use helium that has a much better heat

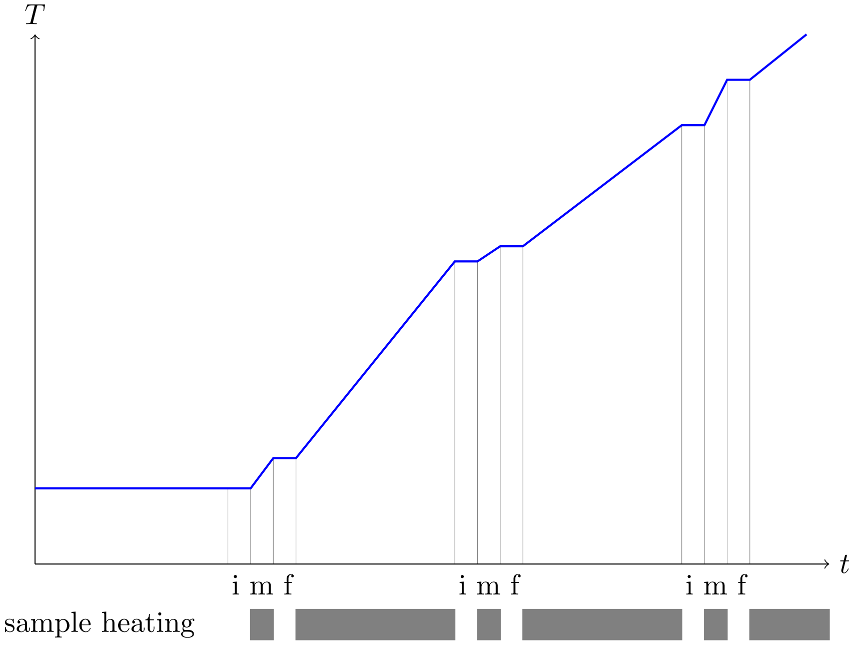

Figure 12: Basic evolution of the temperature during the experiment

conductivity than normal air and because it can be more easily pumped out due to its small molecular weight.

To insert the exchange gas the valve to the vacuum pump needs to be closed and the pump can be shut down. A balloon is attached to a helium gas bottle and filled with helium. Then the balloon is attached to the venting valve and the valve slowly opened. As soon as there is enough helium – a pressure around 30 mbar should suffice – inside the calorimeter the venting valve should be closed again.

After that the calorimeter is lowered into the liquid nitrogen so it is fully covered by it. After about 1 hour the sample should have thermalized to approximately the temperature of the liquid nitrogen. The vacuum pump is started and the corresponding valve opened in order to evacuate the helium from the calorimeter and to start the C_p-measurements. The liquid nitrogen now acts as the heating bath. At the beginning it is important that the calorimeter is almost completely covered by nitrogen, but at higher temperatures this is not required. So don't worry if the nitrogen evaporates during the experiment.

The environment should always have approximately the same temperature as the sample. The heating current should remain constant during one measurement (i.e. from the beginning of the initial period to the end of the final period). The heating power needed to keep the environment at constant temperature can be easily estimated after a few tries. The better Rumford's trick is adhered to the preciser the results.

For the heating power of the environment these approximate values can be considered:

temperature	**situation**	**watt**
$\approx 20°$ C	room temperature	0.0
$100°$ C		4.0
$-196°$ C	calorimeter is completely covered by liquid nitrogen	0
$0°$ C	about half of the calorimeter is covered by liquid nitrogen	1.5

Furthermore the sample and the environment should not be heated up too much: The temperature is easily increased but it can take a long time for the sample to cool down! **Determine the function $C_V(T)$ considering all corrections explained in the previous sections.**

A. Appendix

A.1. Notes

- Please do not open the calorimeter without explicit permission from the assistant.
- The resistance of the heating wires is temperature dependent.
- The voltage on the thermo couples can be amplified 100x, 300x or 1000x.
- The amplifier transfer functions should be calibrated for each amplifier as function of input voltage ($V_{\text{out}} = aV_{\text{in}} + b$) where a is the linear amplification and b is the offset.
- Do not use the power source as input signal for the amplifier!! (Use for example the voltage from the thermocouples, and measure in- and output voltages at different temperatures)
- The computer interface should be calibrated for each channel (is 1 volt on the input also 1 volt in the saved data file?)
- Note that the computer interface has a limited input voltage of approximately $5V$

A.2. Technical details

sample (setup 1): $m = 91.09$ g
sample (setup 2): $m = 91.16$ g
sample (setup 3): $m = 91.02$ g
heating wires: ~ 70 turns of copper-wire, diameter 0.1 mm
$m_{\text{Cu}} \approx 1.85$ g, $\varrho = 8.94\,\frac{\text{g}}{\text{cm}^3}$
teflon: ~ 2 g

A.3. Specific heat capacity of teflon from [8]

T [°K]	c_V $\left[\frac{\mathrm{J}}{\mathrm{g}\cdot\mathrm{K}}\right]$
0	0
5	0.0024
10	0.0182
15	0.0477
20	0.0764
25	0.1016
30	0.1247
35	0.1455
40	0.1647
45	0.1833
50	0.2017
55	0.2198
60	0.2330
65	0.2562
70	0.2745
75	0.2929
80	0.3120
85	0.3312
90	0.3500
95	0.3680
100	0.3857
105	0.4035
110	0.4212
115	0.4380
120	0.4566
125	0.4740
130	0.4910
135	0.5080
140	0.5250
145	0.5423
150	0.5598
155	0.5775
160	0.5975
165	0.6180
170	0.6385

T [°K]	c_V $\left[\frac{\mathrm{J}}{\mathrm{g}\cdot\mathrm{K}}\right]$
175	0.6587
180	0.6772
185	0.6940
190	0.7102
195	0.7257
200	0.7488
205	0.7558
210	0.7701
215	0.7842
220	0.7982
225	0.8120
230	0.8257
235	0.8394
240	0.8533
245	0.8673
250	0.8918
255	0.8971
260	0.9135
265	0.9315
270	0.9526
275	0.9765
280	1.012
310	1.021
315	1.023
320	1.027
325	1.032
330	1.038
335	1.044
340	1.049
345	1.055
350	1.001
355	1.068
360	1.074
365	1.081