

V47

Molar heat capacity

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1 Motivation

The aim of this experiment is to determine the specific heat capacity C of copper and its temperature dependence at low temperatures and room temperature. Therefore, the specific heat capacity at constant pressure C_p is measured and translated to the specific heat capacity at constant volume C_V . Different models to describe the temperature dependency are compared and experimentally tested. These are the classical model, the Einstein model and the Debye model. Furthermore, the *Debye temperature* Θ_D is derived from the experiment's results and compared with the model's theoretical expectations.

2 Theory

The heat capacity of a material describes the amount of heat that is needed to increase the temperature of a certain amount of the material by 1 K. In general, it can be calculated as

$$C = \frac{\delta Q}{\delta T}$$

where δQ is the input heat and δT the change in temperature. Most often the molar heat capacity c^m is used, but also the heat capacity per mass c^{mass} or the heat capacity per volume c^{vol} can be applied. As mentioned before, it is differentiated between heat capacity at constant volume C_V and constant pressure C_p . For C_V the equation

$$C_V = \left. \frac{\delta U}{\delta T} \right|_V \quad (1)$$

can be used to calculate the heat capacity, where U is the internal energy of the system. Experimentally, it is often easier to measure the heat capacity

$$C_p = \left. \frac{\delta Q}{\delta T} \right|_p \quad (2)$$

at constant pressure because most materials expand when heated. The deviation of C_p and C_V can be corrected using

$$C_p - C_V = 9TV\alpha_V^2 B \quad (3)$$

where α_V is the volumetric expansion coefficient and B the so-called bulk module.

2.1 Classical theory of heat capacity

In classical thermodynamics, the equipartition theorem states that the thermal energy of a solid is evenly distributed on its degrees of freedom and every degree of freedom corresponds to $\frac{1}{2}k_B T$ of kinetic and potential energy, respectively. Here, k_B is the Boltzmann constant. Assuming a crystal of N unit cells (1 atom per cell), this results in a total internal energy of

$$U = U^{\text{eq}} + 3N \cdot 2\frac{1}{2}k_B T = U^{\text{eq}} + 3Nk_B T.$$

Using Equation 1 the heat capacity at constant volume reads

$$C_V = 3Nk_B.$$

For the molar heat capacity, the *Dulong-Petit* law

$$c_V^m = 3R \quad (4)$$

can be derived. Here $R = N_A k_B$ is the gas constant and N_A the Avogadro constant (number of atoms in 1 mol). The classical approach leads to a heat capacity that is material- and temperature independent. Experimental results however, show that at low temperatures, the heat capacity is proportional to T^3 and only approaches the classical value for C_V at higher temperatures. Also, a dependence on the material can be noticed in experiments. Quantum mechanical effects have to be taken into account to explain this behaviour.

2.2 The Einstein model

The Einstein approximation was the first theory to describe quantum dynamic effects on heat capacity. The approximation assumes the same frequency ω_E for all $3N$ oscillation modes of the system. Only energies of whole multiples of $\hbar\omega$ can be absorbed or emitted. With this approach

$$\langle U \rangle = 3N\hbar\omega_E \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_E/k_B T}} \right)$$

follows for the internal energy using the Bose-Einstein statistics. The heat capacity will be

$$C_V^E = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \quad (5)$$

where $\Theta_E = \hbar\omega_E/k_B$ is the Einstein temperature. The approximation for low and high temperatures

$$C_V^E = \begin{cases} 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T}, & T \ll \Theta_E \\ 3Nk_B, & T \gg \Theta_E \end{cases}$$

yields the correct result for high temperatures but does not follow the experimental dependency for the low temperature case. This is caused by the assumption that all atoms have the same frequency.

2.3 The Debye model

A better approximation is given by the Debye model, which introduces two fundamental assumptions: 1. All phonon branches are approximated by three (acoustic) branches with a linear dispersion relation $\omega_i = v_i q$. 2. The summation over all possible wave vectors q is replaced by an integration over the first Brillouin zone that can further be simplified to a spherical integration with radius q_D . Because of the requirement that N different states (per branch) have to be included in the sphere and using a volume of $(2\pi/L)^3$ per

state, the wave vector reads $q_D = \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}}$. The Debye Frequency is $\omega_{D,i} = q_D v_i$ where v_i is the speed of sound of the i -th branch. The density of states can be written as

$$D_i(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v_i^3}.$$

Now the internal energy

$$U = \int_0^{\omega_D} \frac{D(\omega)}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

can be calculated. Using the mean speed of sound v_S of the three phonon branches and substituting $x = \hbar v_S q / k_B T$, the heat capacity

$$C_V^D = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (6)$$

can be derived. This can be approximated as

$$C_V^D = \begin{cases} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D}\right)^3, & T \ll \Theta_D \\ 3Nk_B, & T \gg \Theta_D \end{cases}$$

for low and high temperatures respectively. This result includes the classical value for C_V at high temperatures, as well as the experimental observation of a T^3 dependency for low temperatures.

3 Experimental setup and measurement process

The apparatus to determine the heat capacity of copper can be seen in Figure 1. The copper sample can be found in the recipient, which is located in the middle of a Dewar container. It is surrounded by a heating coil that can be used to heat the sample while monitoring the input electric power. Another copper cylinder with a second heating coil is installed around the sample. This is needed to compensate the black body radiation from the sample and prevent heat conduction. The temperature of both copper pieces is measured using Pt-100 resistors connected to ohmmeters. Their resistance is a function of the temperature. The temperature in degrees Celsius can be calculated as

$$T(R) = 0.00134R^2 + 2.296R - 243.02 \quad (7)$$

with the resistor's value R in ohms. A vacuum pump is used to evacuate the recipient. The apparatus can be cooled by filling liquid nitrogen in the Dewar container. During this process, helium is inserted into the recipient through a helium bottle that is also connected to the apparatus.

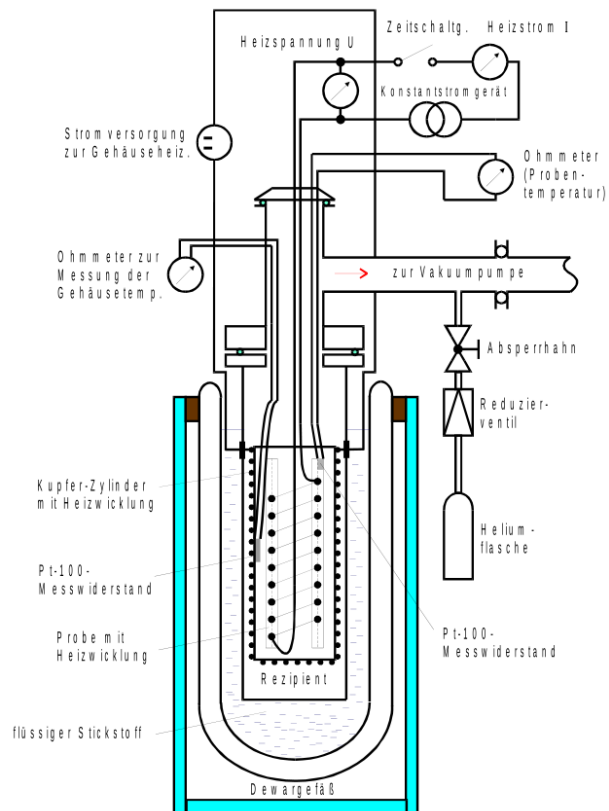


Figure 1: Experimental setup of the measurement of the heat capacity of copper [1].

3.1 Measurement process

First, the recipient is evacuated and filled with helium. Liquid nitrogen is poured into the Dewar container to cool the recipient. When a temperature of 80 K (i.e. $R = 22.6 \text{ m}\Omega$) is reached, the vacuum pump is turned on to keep the experiment at a constant low pressure. The whole cooling process can take up to an hour. Now the apparatus is heated using the heating coils. The inner coil should be set to a current of approx. 160 mA while the outer coil has to be repeatedly adjusted to match the temperature of the inner coil. In steps of 7°C to 11°C the time interval, the sample temperature (resistance), as well as the current and voltage of the heating coil are noted. As a reference table 2 can be used to determine the resistances corresponding to the desired temperature intervals.

T[°C]	-200	-190	-180	-170	-160	-150	-140	-130	-120
R[Ω]	18,44	22,71	27,03	31,28	35,48	39,65	43,80	47,93	52,04
T[°C]	-110	-100	-90	-80	-70	-60	-50	-40	-30
R[Ω]	56,13	60,20	64,25	68,28	72,29	76,28	80,25	84,21	88,17
T[°C]	-20	-10	0	+10	+20	+30	+40		
R[Ω]	92,13	96,07	100	103,90	107,79	111,67	115,54		

Figure 2: Resistor values and corresponding temperatures [1].

The recorded data can be used to calculate the heat capacity at constant pressure C_p of copper.

4 Analysis

The recorded data ist shown in Table 1. The measured resistance of the thermometers is converted to temperatures using Equation 7. To calculate the energy E added in the observed time interval Δt , the current I ist multiplied with both the length of the time interval Δt and the applied voltage U

$$E = I \cdot \Delta t \cdot U. \quad (8)$$

4.1 Heat capacity at constant pressure

A calculation of the values for C_p can be done via Equation 2 resulting in

$$C_p = \frac{M}{m} \frac{E}{\Delta T}, \quad (9)$$

where $M = 63.546 \text{ g/mol}$ is the molar mass of Copper and $m = 342 \text{ g}$ ist the mass of the copper sample used in the experiment.

All the calculated data is also shown in the Table 1.

Table 1: Measured and calculated data used to determine the heat capacity of Copper.
The temperatures are calculated using Equation 7, the added energy is received via Equation 8 and for the values of C_p Equation 9 is used.

$\Delta t / \text{s}$	Measured data			Calculated data			$C_p / \frac{\text{J}}{\text{molK}}$
	R / Ω	I / mA	U / V	E / J	T / K	$T / ^\circ\text{C}$	
-	24.4	158.5	16.63	-	86	-186	-
235	27.0	160.8	16.85	636.7	93	-180	19.24
335	31.3	160.0	16.80	900.5	103	-169	16.39
385	35.5	159.3	16.75	1027.3	113	-159	19.05
405	39.7	159.8	16.80	1087.3	123	-149	20.07
380	43.8	160.1	16.87	1026.3	133	-139	19.32
405	47.9	160.3	16.91	1097.8	143	-129	20.57
345	52.0	160.6	16.95	939.1	153	-120	17.52
435	56.1	160.8	16.97	1187.0	163	-109	22.04
405	60.2	160.9	16.99	1107.1	173	-99	20.46
425	64.3	161.1	17.01	1164.6	183	-89	21.43
455	68.3	161.2	17.03	1249.1	193	-79	23.46
440	72.3	161.2	17.03	1207.9	203	-70	22.58
430	76.3	161.3	17.03	1181.2	213	-60	21.99
460	80.3	161.4	17.04	1265.1	223	-50	23.45
480	84.2	161.4	17.04	1320.1	232	-40	24.99
405	88.2	161.5	17.04	1114.5	243	-30	20.49
425	92.1	161.5	17.04	1169.6	252	-20	21.96
465	96.1	161.5	17.04	1279.7	263	-9	23.33
435	100.0	161.6	17.04	1197.8	273	0	22.30
480	103.9	161.6	17.03	1321.0	283	9	24.50
465	107.8	161.6	17.03	1279.7	293	20	23.63
470	111.7	161.7	17.03	1294.3	303	30	23.81

4.2 Heat capacity at constant volume

The heat capacity at constant volume C_V can be derived by using Equation 3 and the in subsection 4.1 calculated heat capacity at constant pressure. The equation is rearranged to

$$C_V = C_p - 9TV_0\alpha^2 B.$$

The values for the bulk module B and the molar volume V_0 can be found in the literature where as the values for the volumetric expansion α is given in Figure 3. Hence the measured temperatures are not listed directly in the table an estimation for the volumetric expansion coefficient is performed via

$$\alpha(T) = \frac{\alpha_i - \alpha_{i-1}}{T_i - T_{i-1}}(T - T_{i-1}) + \alpha_{i-1}. \quad (10)$$

T [K]	70	80	90	100	110	120	130	140
α [10^{-6} grd $^{-1}$]	7,00	8,50	9,75	10,70	11,50	12,10	12,65	13,15
T [K]	150	160	170	180	190	200	210	220
α [10^{-6} grd $^{-1}$]	13,60	13,90	14,25	14,50	14,75	14,95	15,20	15,40
T [K]	230	240	250	260	270	280	290	300
α [10^{-6} grd $^{-1}$]	15,60	15,75	15,90	16,10	16,25	16,35	16,50	16,65

Figure 3: Values for the volumetric expansion coefficient α of copper. These values and Equation 10 are used to calculate a specific value for each individual temperature T [1].

The used values for the bulk module are

$$B = 140 \times 10^9 \text{ Pa}$$

$$V_0 = \frac{M}{\rho} = 7.092 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

In Table 2 the values for the molar heat capacity with constant pressure and constant volume are given as well as the used volumetric expansion coefficient.

4.3 The Debye temperature of copper

Calculating the Debye temperature θ_D can be achieved by looking up values for $\frac{\theta_D}{T}$ in Figure 5 and multiplying with the temperature T . Only values for a temperature of less than 170 K must be looked at. The results are presented in Table 3.

Table 2: Calculated values for the volumetric expansion coefficient α and the heat capacity for constant pressure C_p and constant volume C_V .

T / K	$\alpha / 10^{-6} \frac{1}{\text{K}}$	$C_p / \frac{\text{J}}{\text{mol K}}$	$C_V / \frac{\text{J}}{\text{mol K}}$
93	10.04	19.24	19.16
103	10.96	16.39	16.28
113	11.70	19.05	18.91
123	12.29	20.07	19.90
133	12.81	19.32	19.12
143	13.29	20.57	20.34
153	13.69	17.52	17.26
163	14.01	22.04	21.75
173	14.33	20.46	20.15
183	14.58	21.43	21.08
193	14.81	23.46	23.08
203	15.03	22.58	22.17
213	15.26	21.99	21.55
223	15.46	23.45	22.98
232	15.64	24.99	24.48
243	15.80	20.49	19.95
252	15.96	21.96	21.38
263	16.15	23.33	22.71
273	16.28	22.30	21.66
283	16.40	24.50	23.82
293	16.55	23.63	22.92
303	16.70	23.81	23.05

Table 3: Calculation of the Debye temperature θ_D using the values for the heat capacity C_V and the corresponding values for $\frac{\theta_D}{T}$ looked up at Figure 5.

T / K	$C_V / \frac{\text{J}}{\text{mol K}}$	$\frac{\theta_D}{T}$	θ_D / K
93	19.16	2.4	223.44
103	16.28	3.1	320.25
113	18.91	2.4	271.98
123	19.90	2.2	271.46
133	19.12	2.4	319.84
143	20.34	2.1	300.68
153	17.26	2.8	428.81
163	21.75	1.7	277.36
Mean			301.73 ± 56.29

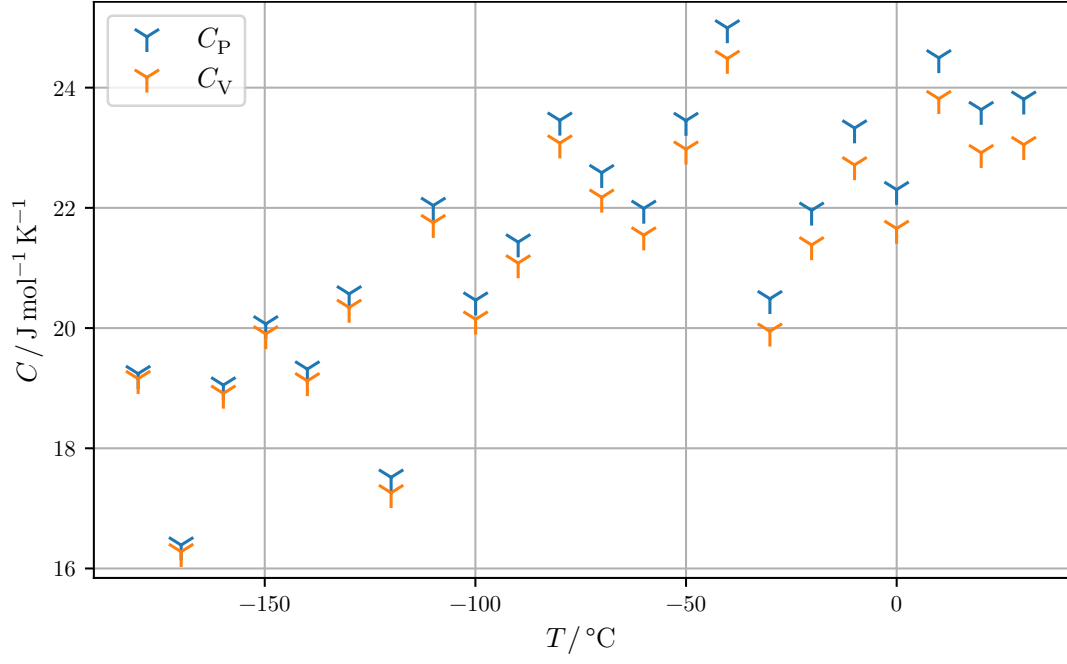


Figure 4: Plot of the heat capacity for constant pressure C_p and constant Volume C_V .

θ_D/T	0	1	2	3	4	5	6	7	8	9
0	24,9430	24,9310	24,8930	24,8310	24,7450	24,6340	24,5000	24,3430	24,1630	23,9610
1	23,7390	23,4970	23,2360	22,9560	22,6600	22,3480	22,0210	21,6800	21,3270	20,9630
2	20,5880	20,2050	19,8140	19,4160	19,0120	18,6040	18,1920	17,7780	17,3630	16,9470
3	16,5310	16,1170	15,7040	15,2940	14,8870	14,4840	14,0860	13,6930	13,3050	12,9230
4	12,5480	12,1790	11,8170	11,4620	11,1150	10,7750	10,4440	10,1190	9,8030	9,4950
5	9,1950	8,9030	8,6190	8,3420	8,0740	7,8140	7,5610	7,3160	7,0780	6,8480
6	6,6250	6,4090	6,2000	5,9980	5,8030	5,6140	5,4310	5,2550	5,0840	4,9195
7	4,7606	4,6071	4,4590	4,3160	4,1781	4,0450	3,9166	3,7927	3,6732	3,5580
8	3,4468	3,3396	3,2362	3,1365	3,0403	2,9476	2,8581	2,7718	2,6886	2,6083
9	2,5309	2,4562	2,3841	2,3146	2,2475	2,1828	2,1203	2,0599	2,0017	1,9455
10	1,8912	1,8388	1,7882	1,7393	1,6920	1,6464	1,6022	1,5596	1,5184	1,4785
11	1,4400	1,4027	1,3667	1,3318	1,2980	1,2654	1,2337	1,2031	1,1735	1,1448
12	1,1170	1,0900	1,0639	1,0386	1,0141	0,9903	0,9672	0,9449	0,9232	0,9021
13	0,8817	0,8618	0,8426	0,8239	0,8058	0,7881	0,7710	0,7544	0,7382	0,7225
14	0,7072	0,6923	0,6779	0,6638	0,6502	0,6368	0,6239	0,6113	0,5990	0,5871
15	0,5755	0,5641	0,5531	0,5424	0,5319	0,5210	0,5117	0,5020	0,4926	0,4834

Figure 5: Table used to calculate the Debye temperature. To get a value for $\frac{\theta_D}{T}$ for a heat capacity C_V a quantity close to the calculated heat capacity C_V needs to be found in the table. The left column is the first digit, the top line is the first decimal digit [1].

4.4 Calculation of the theoretical Debye frequency and Debye temperature

Using the equation for the density of states function

$$Z(\omega)d\omega = \frac{V}{2\pi^2}\omega^2 \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3} \right)$$

the Debye frequency can be calculated as

$$\omega = \left(\frac{18\pi^2 N_A}{V_0} \left(\frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3} \right)^{-1} \right)^{\frac{1}{3}}.$$

Utilizing the Avogadro constant N_A and the values for the longitudinal and transversal phase velocity $v_{\text{long}} = 4.7 \text{ km/s}$ and $v_{\text{trans}} = 2.26 \text{ km/s}$ as well as the molar volume of the sample V_0 the Debye frequency is calculated as

$$\omega_D = 4.35 \times 10^{13} \frac{1}{\text{s}}.$$

With the help of the relation

$$\theta_D = \frac{\hbar\omega_D}{k_B}$$

the theoretical value for the Debye temperature of copper results as

$$\theta_D = 332.18 \text{ K}.$$

5 Discussion

The measured heat capacity plotted in Figure 4 shows increasing values for both C_P and C_V but the slope is not monotonically increasing. There are many saltus in the graph. This can be explained with a low quantity of data but badly adjusted temperature for the outer coil could also be a reason for that.

The Debye temperature is measured as $\theta_{D,\text{exp}} = (301.73 \pm 56.29) \text{ K}$ in the experiment but calculated to be $\theta_{D,\text{theo}} = 332.18 \text{ K}$. This is a deviation of 9.17 %, calculated with

$$\Delta_{\text{rel.}}(\theta_D) = \frac{|\theta_{D,\text{theo}} - \theta_{D,\text{exp}}|}{\theta_{D,\text{theo}}}.$$

The high uncertainty in the measured Debye temperature can be explained with the scattered data for the heat capacity. The looking up data in the given tables is also not that precise and can therefore lead to uncertainties in the data.

References

- [1] V47 - *Temperaturabhängigkeit der Molwärme von Festkörpern*. TU Dortmund.