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Temperature dependence of molar heat of copper

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1 Goal

The goal of this experiment is to measure the molar heat of copper as a function of temperature. To explain the temperature dependence, different models are compared. Finally, the Debye temperature θ_D is determined.

2 Theory

The information in this section is based on [1].

The heat capacity C is the amount of heat δQ needed to raise the temperature of a substance by one degree Kelvin, therefore it is defined as $C = \frac{\delta Q}{\delta T}$. Often the molar heat capacity c_m is used, which is the heat capacity of one mole of a substance. Analogously, the mass heat capacity c_{mass} is the heat capacity of one kilogram of a substance. It is differentiated between the heat capacity at constant volume C_V and the heat capacity at constant pressure C_p . The latter is defined as

$$C_p = \left(\frac{\delta Q}{\delta T} \right) \Big|_p, \quad (1)$$

whereas the former is defined as

$$C_V = \left(\frac{\delta Q}{\delta T} \right) \Big|_V \quad (2)$$

with δU as the change in internal energy. The two capacities are not interchangeable. This is because at a constant volume the heat is used to increase the internal energy, whereas at a constant pressure the heat is also used to do work. Gases expand with increasing temperature and thus do work against the surrounding pressure, which is why the heat capacity at constant pressure is higher than the heat capacity at constant volume ($C_p > C_V$). In solids, however, the expansion is negligible, so that the heat capacities at constant volume and constant pressure are approximately equal. The difference between the two heat capacities is given by

$$C_p - C_V = TV_0 \alpha_V^2 \kappa, \quad (3)$$

with κ being the bulk modulus and α_V the volume expansion coefficient.

2.1 The classical theory of heat capacity

Discussing a system of n unit cells and r atoms per unit cell, the mean internal energy of a system with $N = n \cdot r$ atoms can be calculated using the equipartition theorem as

$$U = U^{eq} + 3Nk_B T, \quad (4)$$

where U^{eq} is the equilibrium energy and k_B is the Boltzmann constant. The heat capacity at constant volume is thus given by the *Dulong-Petit law* as

$$C_V = 3R = 3N_A k_B, \quad (5)$$

where R is the universal gas constant and N_A is Avogadro's number. The Dulong-Petit law is a good approximation for the heat capacity at high temperatures. However, at low temperatures the heat capacity was measured to be lower than predicted by the Dulong-Petit law. This is because quantum effects become more important at low temperatures.

2.2 The Einstein model of heat capacity

The Einstein model was the first model to explain the temperature dependence of the heat capacity at low temperatures using quantum mechanics. The theory describes excitations of an elastic arrangement of atoms as N harmonic oscillators with the same frequency ω_E . It quantizes these excitations using quasi-particles called *phonons* with energy $E_n = \hbar\omega_E$. Using bose-einstein statistics, the mean internal energy of the system can be calculated as

$$\langle U \rangle = 3N\hbar\omega_E \left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1} \right). \quad (6)$$

Thus, the heat capacity at constant volume C_V is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right) \Big|_{V=\text{constant}} = 3N \cdot \frac{(\hbar\omega_E)^2}{k_B T^2} \cdot \frac{\exp\left(\frac{\hbar\omega_E}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1 \right]^2}. \quad (7)$$

Expression (7) can be simplified using the *Einstein-temperature* $\theta_E = \hbar\omega_E/k_B$ as

$$C_V^E = 3Nk_B \left(\frac{\theta_E}{T} \right)^2 \cdot \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left[\exp\left(\frac{\theta_E}{T}\right) - 1 \right]^2}. \quad (8)$$

As approximation for low and high temperatures, the following limits are calculated using equation (8)

$$C_V^E = \begin{cases} 3Nk_B \left(\frac{\theta_E}{T} \right)^2 e^{-\frac{\theta_E}{T}} & , \text{ for } T \ll \theta_E, \\ 3Nk_B & , \text{ for } T \gg \theta_E. \end{cases} \quad (9)$$

The Einstein model is a good approximation for the heat capacity at high temperatures as it approaches the Dulong-Petit law. However, at low temperatures the heat capacity is

$$\lim_{T \rightarrow 0} C_V \propto \exp\left(-\frac{\theta_E}{T}\right) = 0. \quad (10)$$

Thus, the Einstein model does not explain the heat capacity at low temperatures. This is because the model assumes that all phonons have the same frequency, which is not the case as it is differentiated between optical and acoustical phonons. The atoms of a unit cell are all moving in phase for acoustical phonons, whereas they are moving out of phase for optical phonons. The Einstein model only takes the acoustical phonons into account, which is why it is not applicable at low temperatures as their occupation is negligible.

2.3 The Debye model of heat capacity

The Debye model is an extension of the Einstein model and takes the different frequencies of the phonons into account. All phonon branches are considered as three branches with linear dispersion relation $\omega_i = v_i q_i$ with the wave vector q_i of the i -th branch and the speed of sound on the i -th branch v_i . The Debye model only takes the optical phonons into account, which works at low temperatures because the occupation of acoustical phonons is negligible. It further simplifies the summation over all wave vectors q by integrating over the first Brillouin zone. Because, however, areas of constant frequency are sphere surfaces for linear dispersions, the integration is done over a sphere with radius q_D . The wave vector has to be chosen so that the integral has exactly N wave vectors to account for the three branches and thus for the $3N$ oscillation modes. A state in frequency space is given by $V_q = (2\pi/L)^3$, thus follows

$$N \left(\frac{2\pi}{L} \right)^3 = \frac{4}{3} \pi q_D^3 \quad (11)$$

$$\Leftrightarrow q_D = \left(6\pi^2 \frac{N}{V} \right)^{1/3}. \quad (12)$$

The heat capacity in the Debye model follows via the *Debye-temperature* $\theta_D = \frac{\hbar v_s}{k_B} \left(6\pi^2 \frac{N}{V} \right)^{1/3}$ as

$$C_V^D = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (13)$$

with the following substitutions

$$x = \frac{\hbar v_s q}{k_B T}, \quad (14)$$

$$dx = \frac{\hbar v_s}{k_B T} dq. \quad (15)$$

As approximation for low and high temperatures, the following limits are calculated using equation (13)

$$C_V^D = \begin{cases} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D} \right)^3 & , \text{for } T \ll \theta_D, \\ 3Nk_B & , \text{for } T \gg \theta_D. \end{cases} \quad (16)$$

The Debye model reaches the Dulong-Petit law at high temperatures and yields a better approximation at low temperatures than the Einstein model.

Using the relations earlier defined, the amount of phonons N_{ph} in dependence of the temperature can be calculated as

$$N_{\text{Ph}} = \int_0^{\omega_D} D(\omega) \langle n(\omega, T) \rangle d\omega, \quad (17)$$

with the density of states $D(\omega)$ and the occupation number $\langle n(\omega, T) \rangle$. The density of states in the debye model for three dimensional systems is given by

$$D(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{v_s^3}, \quad (18)$$

where crucially v_s denotes the mean speed of sound of all phonon branches. Using the substitutions

$$x = \frac{\hbar\omega}{k_B T}, \quad (19)$$

$$dx = \frac{\hbar d\omega}{k_B T} d\omega, \quad (20)$$

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T}, \quad (21)$$

the phonon number can be written as

$$N_{\text{Ph}} = \frac{3V}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{x_D} \frac{x^2}{e^x - 1} dx. \quad (22)$$

This expression yields the following limits for low and high temperatures

$$N_{\text{Ph}} \propto \begin{cases} T^3 & , \text{for } T \ll \theta_D, \\ T & , \text{for } T \gg \theta_D. \end{cases} \quad (23)$$

3 Experimental setup and procedure

The experiment is conducted as described in the manual [2] with the setup shown in figure 1.

The copper sample is placed inside the recipient that is first evacuated and then filled with helium gas at atmospheric pressure. To cool the sample, the recipient is placed inside a Dewar surrounding it with liquid nitrogen. The temperature is measured using a PT-100 resistor that measures the temperature using the dependence of resistance on temperature. After the sample has reached a temperature of about 80 K, the vacuum pump is turned on again reduce the internal pressure to as low as possible to reduce heat loss to convection. Next, the sample is heated by a heating coil that is controlled by a power supply. The temperature of the sample is again measured using a PT-100 resistor and can be calculated via

$$T = 0.00134 \cdot R^2 + 2.296 \cdot R + 4.095, \quad (24)$$

To further reduce the heat loss, the sample is surrounded by a radiation shield.

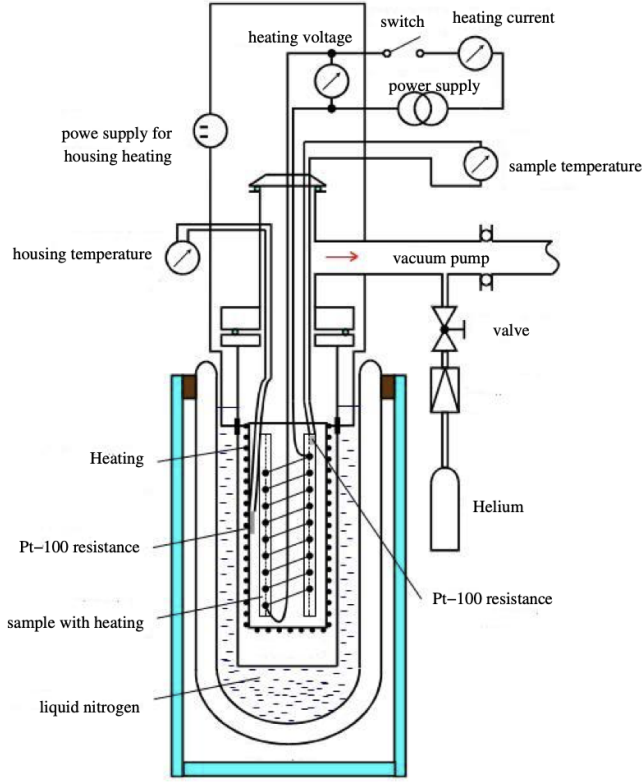


Figure 1: Schematic drawing of the experiment setup [2].

4 Analysis

To compute the isobaric heat capacity C_p , the molar mass of copper $M = 63.546 \frac{\text{g}}{\text{mol}}$, the sample's mass $m = \text{g}$, the energy E that was added to the system and the temperature difference ΔT that was achieved by adding this amount of energy are required.

To get the energy, the voltage U , the current I and the time interval Δt over which energy was added to the system were measured. To get the temperature T of the system, the thermometre's resistance R was measured, since the temperature can then be measured via

$$T(R) = 0.00134R^2 + 2.296R - 243.02 . \quad (25)$$

The resistance steps have been chosen carefully to ensure that ΔT is always 10K. To get the isobaric heat capacity, the measured and computed values have to be plugged into the equation

$$C_p = \frac{M}{m} \frac{E}{\Delta T} . \quad (26)$$

The isochoric heat capacity is related to the isobaric heat capacity via

$$C_V = C_p - 9V_0\alpha^2\kappa T , \quad (27)$$

has has been noted in Equation 3.

Here, $\kappa = 137.8\text{GPa}$ is the bulk module, $V_0 = 7.092 \times 10^6 \frac{\text{m}^3}{\text{mol}}$ the molar volume and α the volumetric expansion. The latter one's values given in [2] do not match the temperatures that have been measured in this experiment. For this reason, a linear interpolation has to be performed, yielding approximate values for α at the measured temperature. These approximates are listed in Table 2

The results for th Table 1.

$T / ^\circ\text{C}$	E / J	$C_p / \frac{\text{J}}{\text{mol}\cdot\text{K}}$	$C_p / \frac{\text{J}}{\text{mol}\cdot\text{K}}$
-180.00	830.96	15.44	15.36
-170.00	927.58	17.24	17.13
-160.00	917.38	17.05	16.91
-150.00	940.83	17.48	17.32
-140.00	959.08	17.82	17.63
-130.00	1026.15	19.07	18.84
-120.00	1062.44	19.74	19.49
-110.00	1141.43	21.21	20.93
-100.00	1152.03	21.41	21.09
-90.00	1113.17	20.68	20.34
-80.00	1110.73	20.64	20.27
-70.00	1084.14	20.14	19.74
-60.00	1301.73	24.19	23.75
-50.00	1711.84	31.81	31.34
-40.00	1309.45	24.33	23.83
-30.00	1331.94	24.75	24.21
-20.00	1241.91	23.08	22.51
-10.00	1186.71	22.05	21.45
-0.00	1084.19	20.15	19.51

Table 1: Values for the isobaric heat capacity C_p and the isochorich heat capacity C_V .

4.1 The Debye Temperature

The Debye temperature can be computed via the table in Figure 2. The first column is the significand and the first line is the mantisse of $\frac{\Theta_D}{T}$. The remaining values are the corresponding heat capacities C_V . Thus, to find a $\frac{\Theta_D}{T}$ -value for a C_V , the closest C_V has to be found in within the table, which makes it possible to read the value from the table.

The Debye temperature can the be derived by simply multiplying the value from the table with the according T . Doing so results in the values depicted in Table 3. Only values $T < 170\text{K}$ have been considered.

The mean value for the Debye-temperature is then $\Theta_D = 330.42 \pm 7.11\text{K}$.

$T / ^\circ\text{C}$	$\alpha / 10^{-6} \frac{1}{\text{K}}$
-180.00	10.04
-170.00	10.96
-160.00	11.70
-150.00	12.29
-140.00	12.81
-130.00	13.29
-120.00	13.69
-110.00	14.01
-100.00	14.33
-90.00	14.58
-80.00	14.81
-70.00	15.03
-60.00	15.26
-50.00	15.46
-40.00	15.64
-30.00	15.80
-20.00	15.96
-10.00	16.15
-0.00	16.28

Table 2: Values for the volumetric expansion α received via linear extrapolation.

$T / ^\circ\text{C}$	θ_D/T	$\theta_D / ^\circ\text{C}$
-180.00	3.30	-594.00
-170.00	2.90	-493.00
-160.00	2.90	-464.00
-150.00	2.80	-420.00
-140.00	2.70	-378.00
-130.00	2.40	-312.00
-120.00	2.30	-276.00
-110.00	1.90	-209.00
-100.00	1.90	-190.00

Table 3: Resulting Debye temperature θ_D

$\frac{\Theta_D}{T}$	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 2: The value of $\frac{\Theta_D}{T}$ can be read off this table. To do so, the closest value for C_V has to be found within the table. Then, $\frac{\Theta_D}{T} = \text{row.column}$

4.2 The Debye Frequency

The Debye frequency is

$$\omega_D = \frac{v_m k_D}{2\pi} . \quad (28)$$

Plugging in the Debye wavenumber

$$k_D = \left(6\pi^2 \frac{N_A}{V_0} \right)^{1/3} \quad (29)$$

and the average speed of sound

$$v_m = \left(\frac{1}{3} \left[2 \frac{1}{v_t^3} + \frac{1}{v_l^3} \right] \right)^{-1/3} \quad (30)$$

into this, the full expression becomes

$$\omega_D = \frac{1}{2\pi} \left(18\pi^2 \frac{N_A}{V_0} \left[2 \frac{1}{v_t^3} + \frac{1}{v_l^3} \right]^{-1} \right)^{1/3} . \quad (31)$$

Here, N_A is the Avogadro-constant, and the velocities are $v_t = 4.7\text{km/h}$ and $v_l = 2.26\text{km/h}$. Plugging all these values in, the final result becomes $\omega_D = 43.39 \cdot 10^{12} \frac{1}{s}$, and thus, via

$$\Theta_D = \frac{\hbar \omega_D}{k_B} \quad (32)$$

the resulting Debye temperature is $\Theta_D = 330.7\text{K}$.

5 Diskussion

The measured heat capacity is $(\Theta_D \pm 7.11)\text{K}$. This almost exactly the theoretical value of 330.7K, with a deviation of only 0.16%.

References

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