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«Измерение энтропии»

Рабочие формулы и исходные данные.

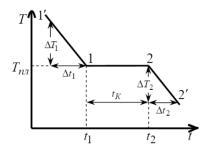


Рис. 1:

В опыте используется сплав массой $M_0=120\ {
m r.}$, который состоит из 60~% олова и 40~% свинца. Также в процессе теплообмена участвует стальная ампула массой $M_a=500$ г. Удельные теплоёмкости данных материалов:

пула массой
$$M_a=500$$
 г. Удельные теплоемкости $C_a(\text{сталь})=460~\frac{\mbox{$\rlap/$\mbox{$\rlap/$$}$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$}\mbox{$\rlap/$

$$C_{Pb} = 128 \frac{\text{Kr} \cdot \text{K}}{\text{Kr} \cdot \text{K}}$$

$$C_0 = 0.6 C_{Sn} + 0.4 C_{Pb} = 188 \frac{\text{Дж}}{\text{K}\Gamma \cdot \text{K}}$$

Удельная теплота кристаллизации сплава:

$$\lambda = \frac{C_0 M_0 + C_a M_a}{M_0} \frac{\Delta T}{\Delta t} t_k \tag{1}$$

, где $\frac{\Delta T}{\Delta t}$ - средняя скорость остывания сплава на участках $1^{'}\to 1$ и $2\to 2^{'}($ Puc. $1);\ t_k$ - время кристаллизации сплава.

Изменение энтропии:

$$S_2 - S_1 = \frac{\lambda M_0}{T_k} \tag{2}$$

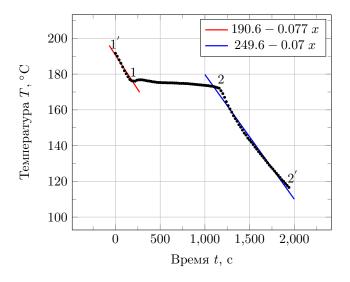
Прямые измерения. Результаты прямых измерений находятся в приложении. Из полученных данных находим:

Время кристаллизации металла $t_k = 960$ с.

Температура кристаллизации $T_k = \frac{176,1+172,1}{2} = 174,1$ (°C)

Экстраполируя данные на отрезках [0,200] и [1160,1940], находим:

$$x_1 = \frac{\Delta T_1}{\Delta t_1} = -0,077 \frac{^{\circ}\text{C}}{c} \left(\frac{\text{K}}{c}\right)$$
$$x_2 = \frac{\Delta T_2}{\Delta t_2} = -0,07 \frac{^{\circ}\text{C}}{c} \left(\frac{\text{K}}{c}\right)$$
$$x = \frac{\Delta T}{\Delta t} = \frac{x_1 + x_2}{2} = -0,0735 \frac{^{\circ}\text{C}}{c} \left(\frac{\text{K}}{c}\right)$$



Расчет результатов косвенных измерений. По формуле (1) вычисляем удельную теплоту кристаллизации сплава:

$$\lambda = \frac{188 \cdot 120 \cdot 10^{-3} + 460 \cdot 0, 5}{120 \cdot 10^{-3}} \cdot 0,0735 \cdot 960 = 148505 \ \left(\frac{\text{Дж}}{\text{кг}}\right)$$

По формуле (2) находим изменение энтропии:

$$S_2 - S_1 = \frac{(-148505) \cdot 120 \cdot 10^{-3}}{174, 1 + 273} = -39,8582 \left(\frac{\Pi \kappa}{K}\right)$$

Погрешность измерений. Оценим погрешность косвенного измерения удельной теплоты кристаллизации по формуле:

$$\begin{split} \delta\lambda &= \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta t_k}{t_k}\right)^2} \\ \Delta t_k &= 20 \text{ c}; \ \Delta x = \frac{\mid x_1 - x_2 \mid}{2} = 0,0035 \ \left(\frac{\mathrm{K}}{c}\right) \\ \delta\lambda &= \sqrt{\left(\frac{0,0035}{0,0735}\right)^2 + \left(\frac{20}{960}\right)^2} = 0,052 \\ \Delta\lambda &= \lambda \, \delta\lambda = 7719 \ \left(\frac{\mathrm{D}_{\mathrm{K}}}{\mathrm{K}\Gamma}\right) \end{split}$$

Погрешность для энтропии:

$$\delta(S_2 - S_1) = \sqrt{\delta \lambda^2 + \left(\frac{\Delta T_k}{T_k}\right)^2 + \left(\frac{\Delta M_0}{M_0}\right)^2}$$

$$\delta(S_2 - S_1) = \sqrt{0,052^2 + \left(\frac{2}{174,1 + 273}\right)^2 + \left(\frac{1}{120}\right)^2} = 0,053$$

$$\Delta(S_2 - S_1) = (S_2 - S_1)\delta(S_2 - S_1) = 2,1$$

Окончательные результаты.

Удельная теплота кристаллизации:

$$\lambda = (148 \pm 8) \cdot 10^3 \, \frac{\text{Дж}}{\text{K}\Gamma}$$

Изменение энтропии:

$$S_2 - S_1 = (-39, 9 \pm 2, 1) \frac{\text{Дж}}{\text{K}}$$

Выводы и анализ результатов.

Мы косвенно измерили удельную теплоту кристаллизации сплава олова и свинца, оценили изменение энтропии при переходе вещества из жидкой фазы в твёрдую. Полученная удельная теплота кристаллизации сильно отличается от ожидаемой величины.

Для чистого олова и свинца $\lambda_{Sn}=60~\frac{\mathrm{K} \square \mathrm{K}}{\mathrm{K} \Gamma};~\lambda_{Pb}=25~\frac{\mathrm{K} \square \mathrm{K}}{\mathrm{K} \Gamma}.$ Ожидаемая величина равна $\lambda=0,6\lambda_{Sn}+0,4\lambda_{Pb}=46~\frac{\mathrm{K} \square \mathrm{K}}{\mathrm{K} \Gamma}.$ По-нашему мнению, свойства сплава сильно отличаются от свойств чистых веществ, и данная оценка не

верна. Но также и возможно, что в нашем опыте существует методическая ошибка.

В ходе кристаллизации сплава энтропия уменьшилась, что соответствует ожиданиям, так как энтропия - это величина, которая характеризует степень хаоса, во время кристаллизации атомы выстраивали упорядоченную решётку, что привело к уменьшению беспорядка. Другими словами $(S=k\ lnP)$, система перешла от более вероятного состояния в менее вероятное.

Приложение

Таблица	1:	Зависимость	температуры	ot	времени

Таблица 1: Зависимость температуры от времени									
t, c	$\mid T, {^{\circ}C} \mid$	t, c	T, °C	t, c	T, $^{\circ}C$	t, c	T, °C		
0	191.6	500	175.3	1000	173.7	1500	143.1		
20	190.0	520	175.2	1020	173.6	1520	141.9		
40	188.0	540	175.2	1040	173.5	1540	140.6		
60	186.1	560	175.2	1060	173.3	1560	139.2		
80	184.0	580	175.1	1080	173.2	1580	138.0		
100	181.9	600	175.1	1100	173.0	1600	136.6		
120	180.2	620	175.1	1120	172.7	1620	135.4		
140	178.5	640	175.1	1140	172.4	1640	134.2		
160	177.0	660	175.0	1160	172.1	1660	133.0		
180	176.3	680	175.0	1180	170.7	1680	131.7		
200	176.1	700	174.9	1200	169.1	1700	130.4		
220	176.1	720	174.8	1220	167.0	1720	129.1		
240	176.6	740	174.8	1240	164.6	1740	128.0		
260	176.8	760	174.8	1260	162.4	1760	126.9		
280	176.8	780	174.7	1280	160.5	1780	125.7		
300	176.8	800	174.7	1300	158.7	1800	124.5		
320	176.6	820	174.6	1320	156.7	1820	123.4		
340	176.4	840	174.5	1340	155.1	1840	122.2		
360	176.2	860	174.4	1360	153.6	1860	120.9		
380	176.1	880	174.3	1380	151.7	1880	120.0		
400	175.9	900	174.2	1400	150.3	1900	118.8		
420	175.7	920	174.1	1420	148.7	1920	117.7		
440	175.6	940	174.0	1440	147.0	1940	116.6		
460	175.4	960	173.9	1460	145.9				
480	175.3	980	173.8	1480	144.2				