

Heat balances and heat capacity calculations

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Abstract We present enthalpy and heat capacity calculations under reversible conditions in which a system is allowed to reach equilibrium after incremental steps in temperature. We focus on the binary systems Ag–Cu and 1,3,5 tri-bromo-benzene and 1,3,5 tri-chloro-benzene and show that due to the compositional effect, thermodynamic properties differ up to an order of magnitude in two-phase regions relative to values in single-phase regions. We demonstrate that Planck's definition of heat capacity needs a minor extension to include the change of phase assemblages due to phase transitions.

Keywords Enthalpy · Heat capacity · Thermal expansivity · Thermodynamics

Introduction: definition of the heat capacity at constant volume or at constant pressure

The heat capacity is a property occurring in the calculation of heat exchange between a system and its surroundings

Dedicated to Professor Su-II Pyun on the occasion of his 65th birthday

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when it changes from one state to a state with different thermodynamic conditions. Because heat exchange is common in industrial processes, knowledge of the heat capacity is valuable in engineering practice. Therefore, it is not surprising that the definition of heat capacity of a system is related to measurable quantities. In words, it is defined as the heat needed to raise the temperature of that system by 1° while keeping the volume, V , or the pressure, P , at a constant value. Although heat is not a state function, it is possible to express the heat capacity as a temperature derivative of the state functions energy and enthalpy, respectively. In the first case, when heat is added to a system at constant volume, the system is unable to perform work by expanding its volume. The result is that the internal energy of the system increases, leading to an increase of the temperature. The first law of thermodynamics relates energy U , heat q , and work as:

$$dU = dq - PdV. \quad (1)$$

The heat capacity at constant volume, C_V , is expressed as the temperature derivative of the energy state function:

$$C_V = \left(\frac{\partial q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (2)$$

In the second case, when heat is added to the system at constant pressure, the system performs work by volume expansion. Simultaneously, the internal energy increases, leading to a rise in the temperature. Using Eq. 1, the heat capacity at constant pressure, C_P , is given by:

$$C_P = \left(\frac{\partial q}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (3)$$

By using the definition of the state function enthalpy, $H = U + PV$, the heat capacity is expressed as:

$$C_P = \left(\frac{\partial q}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (4)$$

The practical application of Eq. 4 is that when the heat capacity of a material is known, it is possible to calculate the heat involved when a system is transferred from an initial temperature to a temperature different from the initial state. Alternatively, it is possible to calculate the heat exchange of a system with its surroundings when it is subjected to a change in temperature.

In common practice, it appears that the heat capacity, C_P , is not a universal constant applicable to all materials. For a specific material, its value depends on pressure–temperature conditions. The temperature dependence of the heat capacity was a hot debate at the turn of the last century before the advent of quantum mechanics. At that time, classical mechanics, described by Newtonian laws of physics, predicted that heat capacity at constant volume, C_V , is a constant depending only on the number of atoms in the molecular formula. This constant is nowadays well known as the du Long–Petit limit at infinite temperature. In his historical paper, Einstein [3] showed, by using a simple monochromatic vibrational model, that C_V for solid substances is not constant for all materials and that for a specific material, it depends on temperature. The groundbreaking outcome of his theory was that it explained the experimental evidence that heat capacity at constant volume for a solid substance changes from 0 at 0 K to the value $3nR$ at infinitely high temperature, with n being the number of atoms in the molecular formula and R being the gas constant. Einstein’s vibrational theory was later improved by Debye [2] and Born and von Karman [1] to represent the temperature behavior of heat capacity to engineering accuracy. The change of the heat capacity at constant volume with temperature has a direct impact on the heat capacity at constant pressure. Thermodynamic theory evidences that

$$C_P = C_V + \alpha^2 KVT, \quad (5)$$

where α denotes the thermal expansivity, K represents the isothermal bulk modulus, and V stands for the volume of

the system. Table 1 shows for three substances the values of C_P and C_V . The table indicates that the last term in Eq. 5 appears to be much smaller compared to C_V and that the temperature behavior of C_P is mostly determined by that of C_V . Figure 1 shows for Mg_2SiO_4 the temperature behavior of C_P and C_V .

In the “Heat capacity and phase transitions” section, we present a classical definition of heat capacity, which we apply in “Heat capacity in multiphase regions” section to multiphase regions of the system Ag–Cu. In “Measurement and relevance of the compositional effect” section, we show that for the system 1,3,5 tri-bromo-benzene–1,3,5 trichloro-benzene, the compositional effect on heat capacity is well elaborated experimentally and that calculations including the compositional effect have implications for the geophysical field of mantle convection.

Heat capacity and phase transitions

Because the definition of the heat capacity involves a differential quotient, it is obvious that a difficulty arises in its evaluation when a phase transition occurs. Suppose that, within 1° of temperature increase, a phase transition occurs than one might argue that the value of C_P evaluated from Eq. 4 is incorrect because it does not include the enthalpy of transformation. The calculation of heat capacity when phase transitions are involved is not trivial, and it is instructive to explore the definition of the heat capacity in such a case in more detail. For this purpose, we explore the definition of C_P given by Max Planck [10]. In his book “Thermodynamik” (§53 in Section 1, Chap. 3, translation by one of the authors), he defines heat capacity as follows.

“While in general the heat capacity changes steadily with temperature, there are for each substance, under a given outside pressure, certain singular temperature points at which with other properties also the heat capacity becomes discontinuous. At these points, an amount of heat added from outside will not go into the body as a whole but only partially and it will not serve to raise the temperature but change the state of aggregation, this being melting, evaporation, or sublimation, depending upon whether the substance goes from solid to liquid, or from liquid to

Table 1 Heat capacity at constant pressure and at constant volume for gold, periclase, and forsterite expressed in joule-per kelvin per-mole

Substance	T_m (K)	C_P ($T = 300$ K)	C_V ($T = 300$ K)	$\left(\frac{C_P - C_V}{C_V} \right)$ ($T = 300$ K) (%)	C_P ($T = 2/3 T_m$)	C_V ($T = 2/3 T_m$)	$\left(\frac{C_P - C_V}{C_V} \right)$ ($T = 2/3 T_m$) (%)
Au	1,337.33	25.48	24.55	3.81	28.20	24.91	13.22
MgO	3,173	36.91	36.43	1.32	59.62	50.30	18.52
Mg_2SiO_4	2,168	118.96	117.76	1.02	187.17	174.36	7.35

The data for gold were taken from the paper of Fei et al. [4], and those of periclase and forsterite were from the studies of Jacobs et al. [7] and Jacobs and de Jong [6]. T_m represents the melting temperature of a substance.

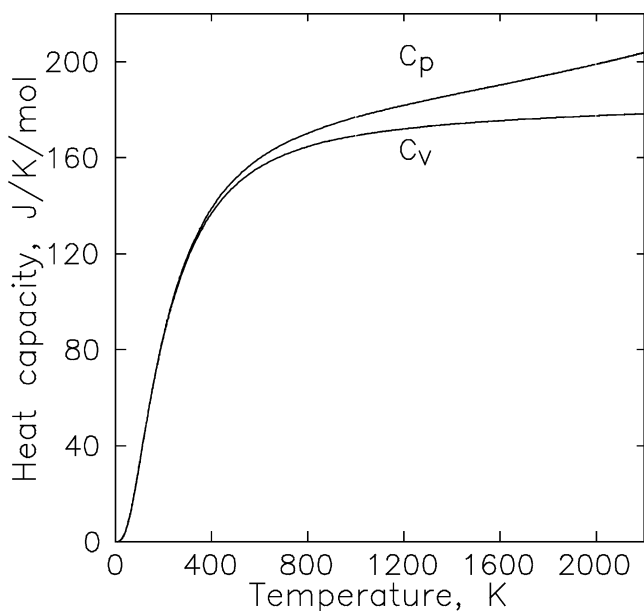


Fig. 1 Heat capacities of Mg_2SiO_4 , forsterite at 1 bar pressure, resulting from a thermodynamic evaluation by Jacobs and de Jong [6]

gaseous, or from solid to gaseous. Only after the whole body at the given temperature has become homogeneous again in the new state of aggregation, the temperature will rise again on continued heating and a heat capacity can be defined again.”

The definition stated by Planck [10] clearly demonstrates that heat capacity cannot be defined at singular points of phase transitions, such as in the melting point of pure silver. Figure 2a shows that the enthalpy behaves discontinuously at the melting point, and therefore its temperature derivative is undefined. Figure 2b shows the corresponding heat capacity, and the two circles in this plot indicate that C_p is undefined in these points. However, when a material has been transformed to a homogeneous phase, such as liquid, it is possible to define values for heat capacity. At the time that Planck wrote his considerations about heat and heat capacity, the calculation of thermodynamic properties in multiphase regions of multicomponent systems was not a common practice as it is nowadays. Therefore, we elucidate the thermodynamic definition of heat capacity for multiphase regions in more detail, respecting the definition given by Planck.

Heat capacity in multiphase regions

To make points clear, we investigate the behavior of enthalpy and heat capacity as a function of temperature in the binary metal alloy system Ag–Cu, for which a thermodynamic description is available, representing 1 bar thermodynamic experimental data. The eutectic phase diagram of this system and calculated using the SGTE

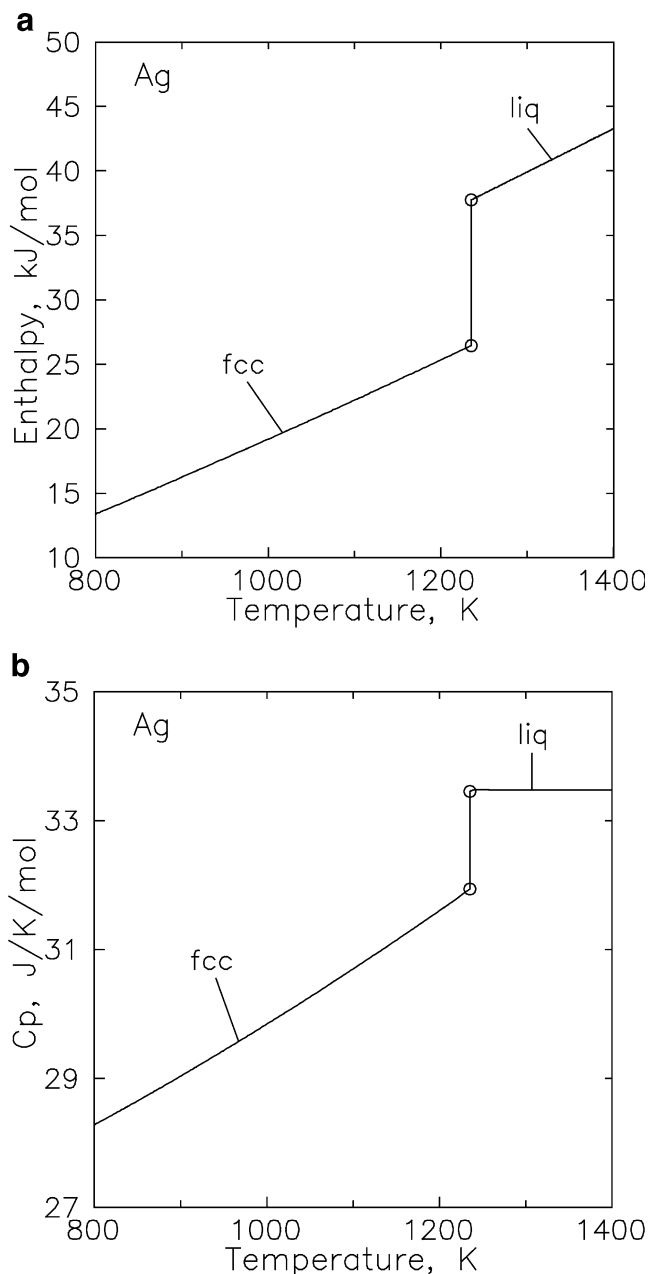


Fig. 2 **a** Enthalpy of silver at 1 bar pressure. The circles in the plot denote points at which the temperature derivative of the enthalpy is undefined. **b** Heat capacity of silver at 1 bar pressure. Circles in the plot denote points at which the temperature derivative of the enthalpy and therefore the heat capacity is undefined

database [11] is plotted in Fig. 3. In this diagram, we have selected two overall compositions. The first overall composition is the eutectic composition.

Figure 4 shows that the calculated enthalpy behaves discontinuously at the eutectic temperature. This behavior is similar to that for the melting of a pure element, such as Ag, depicted in Fig. 2. Therefore, C_p cannot be defined at the eutectic temperature, commensurate with the statements of Planck [10].

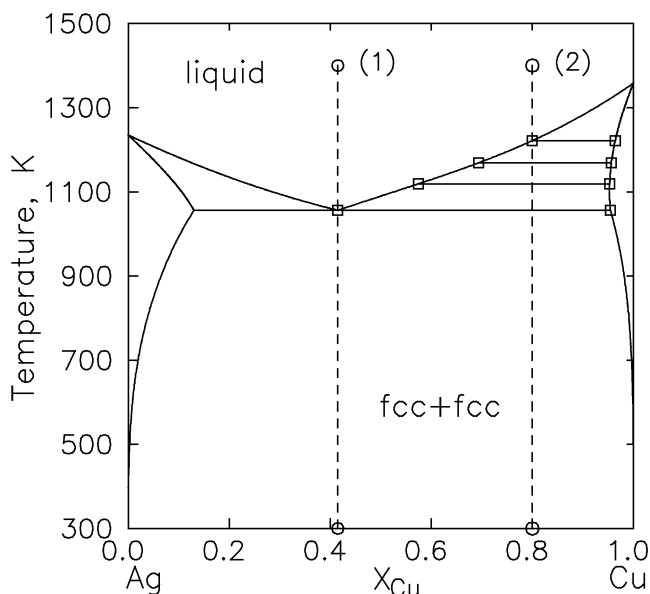


Fig. 3 Phase diagram of the system Ag–Cu. Two paths denoted by (1) and (2), respectively, are defined along which enthalpy and heat capacity were calculated. The horizontal lines in the upper-right part of the diagram are tie lines

The second overall composition is a mixture of 0.2 mol Ag and 0.8 mol Cu. The enthalpy of a multiphase region is generally obtained as the sum of the enthalpy contribution of each phase, which takes part in the equilibrium:

$$H = \sum_{\varphi} n_{\varphi} H^{\varphi}, \tag{6}$$

with n_{φ} being the fraction of Ag and Cu atoms in phase φ relative to the total number, N , of atoms in the system.

The heat capacity is derived by applying its definition given by Eq. 4:

$$\begin{aligned} C_P &= \sum_{\varphi} \left(n_{\varphi} \left(\frac{\partial H^{\varphi}}{\partial T} \right)_P \right) + \sum_{\varphi} \left(H^{\varphi} \left(\frac{\partial n_{\varphi}}{\partial T} \right)_P \right) \\ &= \sum_{\varphi} (n_{\varphi} C_P^{\varphi}) + \sum_{\varphi} \left(H^{\varphi} \left(\frac{\partial n_{\varphi}}{\partial T} \right)_P \right). \end{aligned} \tag{7}$$

For a two-phase region, such as liquid + fcc, the heat capacity is thus written as:

$$\begin{aligned} C_P &= n_{\text{liq}} C_P^{\text{liq}} + n_{\text{fcc}} C_P^{\text{fcc}} + H^{\text{liq}} \left(\frac{\partial n_{\text{liq}}}{\partial T} \right)_P \\ &\quad + H^{\text{fcc}} \left(\frac{\partial n_{\text{fcc}}}{\partial T} \right)_P. \end{aligned} \tag{8}$$

$C_P^{\text{liq}}(T, x^{\text{liq}})$ and $C_P^{\text{fcc}}(T, x^{\text{fcc}})$ represent the heat capacities of the liquid and fcc phases, respectively, at their equilibrium compositions. The first two terms on the right-hand side of Eq. 8 express the classical sum of the weighted heat capacities of the phases at the temperature of interest. The last two terms are related to the change of

equilibrium compositions when the temperature of the system changes. That can be demonstrated by making use of the lever rule. The fractions n_{liq} and n_{fcc} are written as:

$$n_{\text{liq}} = \frac{x^{\text{fcc}} - x}{x^{\text{fcc}} - x^{\text{liq}}} \quad \text{and} \quad n_{\text{liq}} + n_{\text{fcc}} = 1, \tag{9}$$

where x^{fcc} and x^{liq} are the equilibrium mole fractions, respectively, and x is the overall composition. The tie lines in Fig. 3 indicate that on heating, the equilibrium compositions change with temperature, provided that the system responds fast enough to establish equilibrium on the action of incremental heat input. The combination of Eqs. 8 and 9 indicates that the heat capacity of the composite material contains contributions related to the slopes of phase boundaries. These slopes are given by the so-called van der Waals equations (see, e.g., the work of Oonk [9]). For two-phase equilibria in binary systems, and for the solid–liquid equilibria in the system Ag–Cu in particular, they are given by:

$$\left(\frac{\partial x^{\text{liq}}}{\partial T} \right)_P = \frac{\left(\frac{\partial S^{\text{liq}}}{\partial x^{\text{liq}}} \right)_{P,T} - \frac{S^{\text{fcc}} - S^{\text{liq}}}{x^{\text{fcc}} - x^{\text{liq}}}}{\left(\frac{\partial^2 G^{\text{liq}}}{\partial (x^{\text{liq}})^2} \right)_{P,T}} \tag{10}$$

$$\left(\frac{\partial x^{\text{fcc}}}{\partial T} \right)_P = \frac{\left(\frac{\partial S^{\text{fcc}}}{\partial x^{\text{fcc}}} \right)_{P,T} - \frac{S^{\text{fcc}} - S^{\text{liq}}}{x^{\text{fcc}} - x^{\text{liq}}}}{\left(\frac{\partial^2 G^{\text{fcc}}}{\partial (x^{\text{fcc}})^2} \right)_{P,T}} \tag{11}$$

Equations 10 and 11 show that the slopes of phase boundary curves are related to the Gibbs energy functions

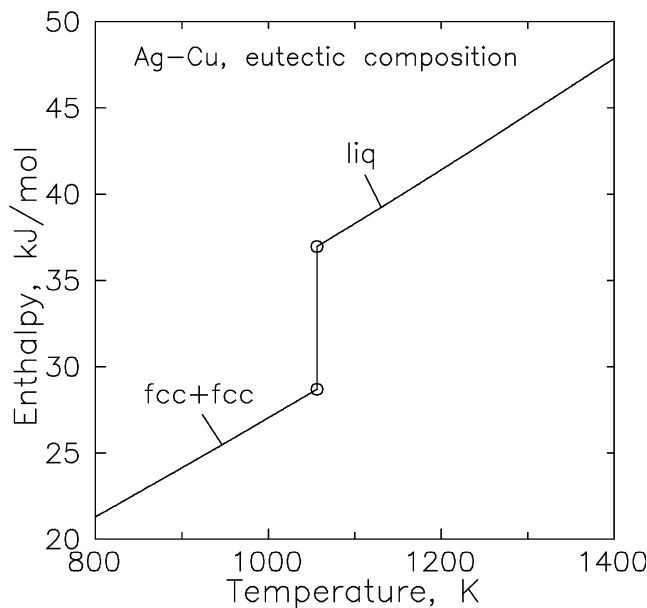


Fig. 4 Enthalpy as a function of temperature at 1 bar pressure of a composite material consisting of Ag and Cu at eutectic composition. Circles in the plot denote points at which the temperature derivative of the enthalpy is undefined

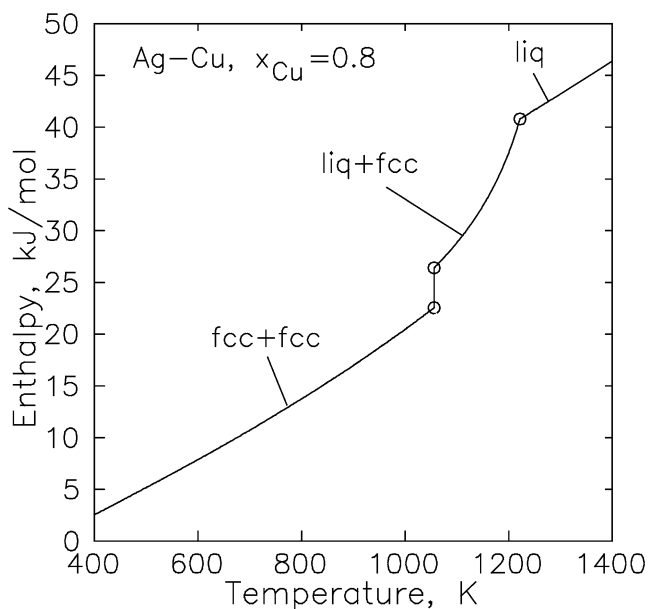


Fig. 5 Enthalpy as a function of temperature at 1 bar pressure of a composite material consisting of Ag and Cu at $x_{Cu}=0.8$. Circles in the plot denote points at which the temperature derivative of the enthalpy is undefined

of the liquid and fcc phases. In the case of the system Ag–Cu, the expressions for the Gibbs energy functions can be written explicitly (SGTE Solution database [11]). Therefore, an explicit expression can be written for the heat capacity of the composite material. In the case of ternary and higher-order systems or in the case that the Gibbs

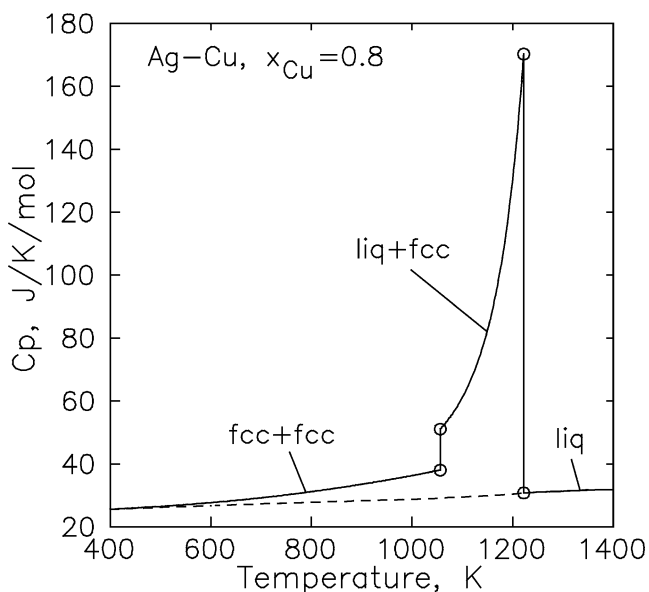


Fig. 6 Heat capacity, C_p , as a function of temperature at 1 bar pressure of a composite material consisting of Ag and Cu at $x_{Cu}=0.8$. Circles in the plot denote points at which the temperature derivative of the enthalpy and therefore the C_p is undefined. The dashed curve represents the heat capacity contribution of the first two terms in Eq. 8. The solid curve represents the complete expression given by Eq. 8

energy functions are nonanalytical functions of composition, it is easier to calculate heat capacity from Eqs. 4 and 6 in a numerical way.

Figure 5 shows the calculated enthalpy for the composite material. The behavior of the enthalpy is clearly different from that given in Figs. 1 and 3 for pure Ag and the eutectic composition, respectively. It is also clear that inside the two-phase regions liquid + fcc and fcc + fcc, a heat capacity can be defined, commensurate with the definition given by Planck [10]. The points at which this is not possible are marked with circles. These points are associated with the eutectic temperature and a point on the liquidus. We have discussed the eutectic case above. In the vicinity of the liquidus, the temperature derivative of the enthalpy above and below the liquidus temperature, T_l , differs. This is expressed mathematically as:

$$\lim_{T \downarrow T_l} \left(\frac{\partial H}{\partial T} \right)_P \neq \lim_{T \uparrow T_l} \left(\frac{\partial H}{\partial T} \right)_P, \quad (12)$$

indicating that C_p is undefined at $T = T_l$. Figure 6 shows that the corresponding heat capacity derived from the enthalpy in Fig. 5 shows a large peak. That peak in the heat capacity is due to the compositional effect given by the last two terms in Eq. 8. The dashed curve in Fig. 6 was calculated by excluding the last two terms in Eq. 8. In the miscibility gap region, the compositional effect of the last two terms increases with temperature. As shown in Fig. 3, the equilibrium compositions show a larger change at the same temperature increment, which is accompanied with a larger change in absolute values of the phase boundary slopes. In the liquid + fcc region, this effect is much larger due to the large change in liquid composition when

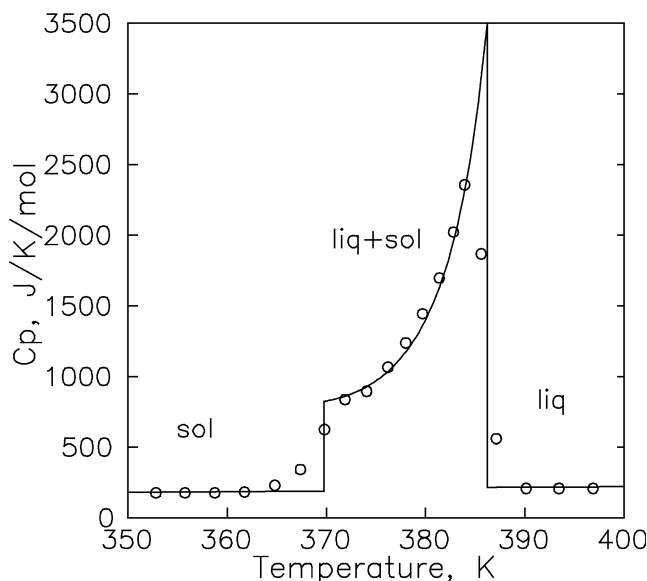


Fig. 7 Calculated heat capacity for an overall composition of 0.8 mol of 1,3,5 tri-bromo-benzene and 0.2 mol of 1,3,5 tri-chloro-benzene. Experimental uncertainty is smaller than the size of the symbols

temperature increases. In this region, the heat capacity including the compositional effect reaches values about seven times larger than excluding it.

Measurement and relevance of the compositional effect

Van der Linde [12], using adiabatic calorimetry, has described an elaborate investigation to this effect. The purpose of that investigation was to determine accurate phase boundary curves in the system 1,3,5 chloro-benzene + 1,3,5 bromo-benzene because the experimental peritectic phase diagram of Maiga [8] appeared to be thermodynamically inconsistent. To this end, Van der Linde [12] measured heat capacity as function of temperature for a series of overall compositions. From these measurements, Gibbs energies of the liquid and solid phases were established, consistent with experimental phase boundary data revealing that the phase diagram is a simple two-phase loop. An example of such measurement is given in Fig. 7.

Van der Linde [12] carried out his measurements by increasing the temperature such that after each step in temperature, equilibrium was achieved. To represent heat capacity data to within experimental uncertainty, he refined the thermodynamic model by introducing a statistical precipitation model. Figure 7 indicates that the effect of such a refinement is small and that the main trend of heat capacity is covered by a classical thermodynamic description.

A field in which equilibrium calculation is important is that of mantle convection in geophysics. Because material transport in the Earth is slow, typically of the order of 1 cm/year, it is plausible to assume that materials involved in a phase transition are in a local state of equilibrium. The governing equations representing material and energy transport in the Earth's mantle contain three thermodynamic properties, heat capacity, thermal expansivity, and density. As has been demonstrated by Jacobs and de Jong [5], thermal expansivity shows similar behavior in multiphase regions because the volume of the composite material is written in a similar way as the enthalpy. It was shown that thermal expansivity reaches values between 6 and 23 times the values in single-phase regions in the solid-state $\text{Mg}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$ system. The transition zone in the Earth, between 400 and 670 km depth, consists of solid-state multiphase regions. Because heat capacity and thermal expansivity appear explicitly in the transport equations, an accurate knowledge of these properties in pressure–temperature space is important for deriving composition, heat budget, and thermal evolution of the Earth mantle.

It should be stressed that the compositional effect on heat capacity results from equilibrium calculations. In each incremental step in temperature, the system is allowed to reach equilibrium. It is therefore obvious that in types of

measurements where no equilibrium is achieved in these incremental steps in temperature, due to, e.g., a low mobility of atoms or molecules, the effect on heat capacity could be very different.

In line of the above observations, the statement of Planck [10] should be modified slightly to incorporate the change to another phase field. In his second and last sentence, the part “state of aggregation” should be replaced by “state of aggregation or phase assemblage”.

Conclusions

The compositional effect on heat capacity in equilibrium calculations is significant in cases where the system is allowed to reach equilibrium after incremental steps in temperature or pressure. For the binary systems Ag–Cu and 1,3,5 tri-bromo-benzene–1,3,5 tri-chloro-benzene, we have shown that heat capacity in two-phase regions reaches values seven and ten times larger, respectively, relative to single-phase regions.

In engineering practice, heat capacity calculated by a thermodynamic model, resulting from equilibrium calculations, may differ from the experimentally established one because the response time is not small enough for the system to achieve equilibrium on the action of incremental heat input.

We demonstrated that Planck's definition of heat capacity needs a minor extension to include the change of phase assemblages due to phase transitions.

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