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PHASE TRANSITIONS AND THERMODYNAMIC PROPERTIES OF ANHYDROUS CAFFEINE*

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Caffeine has been found to display a low-temperature β- and a high-temperature α-modification. By quantitative DTA the following data were determined: transformation temperature 141±2°; enthalpy of transition 4.03±0.1 kJ · mole^{-1}; enthalpy of fusion 21.6±0.5 kJ · mole^{-1}; molar heat capacity

ϑ/°C	100 (β)	100 (α)	150 (α)	200 (α)
C_p°/J · K^{-1} · mole^{-1}	271±9	287±10	309±11	338±10

in good accord with drop-calorimetric data. For the constants of the equation $\log(p/\mathrm{Pa}) = -A/T + B$, static vapour pressure measurements on liquid and solid α-caffeine, and effusion measurements on solid β-caffeine yielded:

$A = 3918 \pm 37; 5223 \pm 28; 5781 \pm 35\ \mathrm{K}^{-1}$
$B = 11.143 \pm 0.072;\ 13.697 \pm 0.057;\ 15.031 \pm 0.113.$

The evaporation coefficient of β-caffeine is 0.17±0.03.

Caffeine (Fig. 1) is an important constituent of many foodstuffs, beverages and pharmaceuticals. The main source of caffeine is coffee, which contains between 0.8 % (Arabica Santos) and 2.5 % (Robusta Angola), and from which it is extracted to obtain decaffeinated coffee [1]. For the improvement of this process, caffeine purification and use the determination of unknown data and the improvement of reported data on caffeine became necessary. The present paper is devoted to anhydrous caffeine; work on the properties of caffeine hydrate and aqueous solutions of caffeine is in progress.

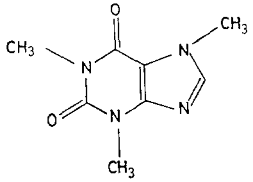

Fig. 1. Caffeine

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Characterization of caffeine

Caffeine (nearly anhydrous, DAB 7, obtained from HAG AG, Bremen) was dried further in vacuo for 24 hours at 120° over 3Å molecular sieve, purified by zone melting under argon, resublimed in high vacuum, and tempered for a sufficient time at 80–120°. The melting point determined was 236.1 ± 0.2° (cf. Ishii *et al.*, who reported 237.19° as the melting point of their "100% pure caffeine" [2]). Purity determination by analysis of the melting peak using quantitative DTA [3] showed that the total molar amount of impurities was certainly less than 0.1%. No impurities could be detected by thin-layer chromatography.

After purification, caffeine is present as the metastable high-temperature α-modification, which at ambient temperature converts only very slowly to the stable β-modification (after storage for one year, a sample was not yet fully converted). The transformation can be greatly accelerated by tempering: after several days at 130°, sublimed caffeine is completely converted to the low-temperature β-modification. Controlled experiments showed that the conversion starts from the crystal surfaces.

Calorimetric measurements and results

The calorimetric measurements were performed using two different instruments for quantitative DTA, namely the Du Pont 990 Thermal Analyzer with cell Base Module II and DSC-cell [4], and the differential heat flux calorimeter MCB by Thermanalyse [5]. The calorimeters were calibrated using the heat of fusion of tin ($\Delta H_f^\circ = 7.195 \pm 0.007$ kJ mole^{-1} [6]). The temperature-dependence of the calibration factor of the MCB calorimeter was determined with the built-in electric heaters using a timer and constant-current source. The heating rates were 10 K min^{-1} (Du Pont) and 1 K min^{-1} (MCB). The samples were encapsulated in gastight (hermetic) capsules and had an absolute mass of 10–30 mg, determined

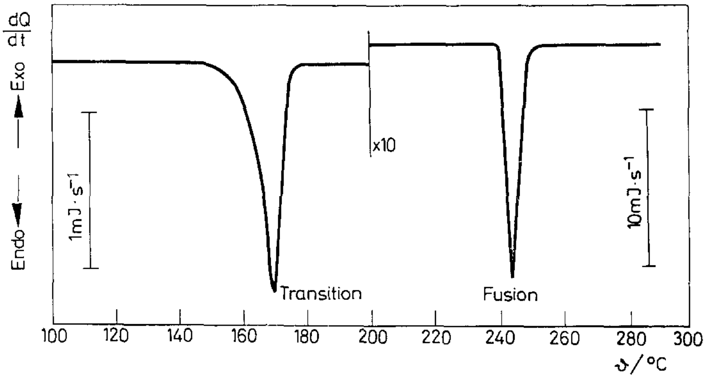

Fig. 2. DTA curve of β-caffeine (heating rate: 10 · min^{-1})

on a microbalance to ±0.01 mg. Peak areas were determined with a roll-planimeter (Ott, Kempten) and/or an electronic integrator (Varianmat, Bremen) and evaluated after Adam and Müller [7]. The enthalpy of fusion and the temperature of the $\beta \rightarrow \alpha$ transition were determined with both instruments, whereas the enthalpy of transition and the molar heat capacities were measured with the Du Pont apparatus using the enthalpy of fusion of caffeine as an internal standard.

The results of our calorimetric determinations by quantitative DTA are compiled in Table 1, together with the literature data, which are scarce. Because of the low transformation rate, the DTA curve of the $\beta \rightarrow \alpha$ transition does not show a very sharp peak onset (cf. Fig. 2), but certainly corresponds to a first-order phase transition, as the Debye–Scherrer diagrams of the two phases exhibit distinctive differences. This is in accord with preliminary observations reported by Grabowska and Kaliszan [8] and by Masse et al. [9]. Although not all details of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions have yet been clarified, the transformation temperature is certainly 141 ± 2°. This temperature was observed with caffeine crystals grown under near-equilibrium conditions, with crystals obtained from

Table 1

Results of calorimetric measurements

Enthalpy of fusion ΔH_f°/kJ · mole^{-1}	21.6±0.5		MCB	(*)
	20.1±0.7		Du Pont	(*)
	23.5		difference of $\overline{\Delta H_v}$ and ΔH_s at T_f	(*)
	22.4		cryoscopic measurements	(2)
Transition temperature ϑ_t/°C	141±2		MCB, Du Pont	(*)
	140±2		TMA Du Pont	
Enthalpy of transition ΔH_t°/kJ · mole^{-1}	4.03±0.1		Du Pont ($\Delta H_f^\circ = 21.6$ kJ · mole^{-1} as internal standard)	(*)
Molar heat capacity C_p°/J · mole^{-1} · K^{-1}	254	25°	estimated by Kopp's rule	(*)
	232	25°	extrap. from QDTA measurements, β-caffeine	(*)
	247	25°	estim. from C_p° of xanthine	(11)
	228	25°	estim. from dropcalorimetric measurements, β-caffeine	(*, 12)
	(215)	25°		(10)
	271 ± 9	100°	Du Pont, β-caffeine	(*)
	281	100°	dropcal., β-caffeine	(*, 12)
	(242)	100°		(10)
	287 ± 10	100°	Du Pont, metastable α-caffeine	(*)
	285	100°	dropcal., metastable α-caffeine	(*, 12)
	309 ± 11	150°	Du Pont, α-caffeine	(*)
	314	150°	dropcal., α-caffeine	(*, 12)
	338 ± 10	200°	Du Pont, α-caffeine	(*)
	343	200°	dropcal., α-caffeine	(*, 12)

Remarks: (*) = this work
The uncertainties given are standard deviations.

slow high-temperature sublimation (heating at 90°, cooling at 70°), and with tempered crystals (see section on characterization of caffeine). Additional TMA measurements yielded $\vartheta_t = 140 \pm 2°$ and a distinctive change in volume, characteristic for a first order transition.

No literature data on ΔH_t° for the transformation are available. The enthalpy of fusion given here compares well with that obtained by Ishii et al. from cryoscopic measurements on the system caffeine/theophylline [2].

The C_p° data of Gabets et al. listed in Table 1 were taken from a small figure in their paper [10], are correspondingly uncertain, and are thus given in parentheses. Stern and Beeninga estimated their C_p° value at 25° from the measured C_p° of xanthine correcting for the additional methyl groups [11]. At our suggestion, Klinge [12] performed drop-calorimetric measurements on C_p° by the method of upper varied temperature ϑ, using our samples. The drop-calorimeter temperature was $\vartheta_0 = 20°$ in all cases. $C_p^\circ(\vartheta)$ was calculated from

$$C_p^\circ(\vartheta) = \overline{C}_p^\circ(\vartheta) + \frac{\overline{C_p^\circ(\vartheta)}}{\partial\vartheta}(\vartheta - \vartheta_0), \tag{1}$$

using a least squares fit of a polynomial to the measured data $\overline{C}_p^\circ(\vartheta)$. The data are in good accord with our values determined by quantitative DTA.

Vapour pressure measurements

Except for some general and qualitative statements, no information on the vaporization behavior of caffeine is to be found in the literature [13]. We have determined the vapour pressures over solid α-caffeine and over liquid caffeine in the range 170–250° with two degasable mercury manometers, one of which is shown in Fig. 3, while the other is described in detail in [14]. The caffeine and mercury were thoroughly degassed by multiple resublimation or boiling in high vacuum prior to measurement. During measurements, a small residual gas pressure built up owing to minute decomposition of caffeine (13 Pa at ambient temperature after about 12 hours), which was taken into account as the temperature-dependent pressure of an ideal gas.

The manometers were thermostated with a silicone fluid temperature bath controlled to ±0.1°. Each pressure value is the mean of three measurements. These were made with rising and falling temperature, with no detectable hysteresis. The uncertainty of the vapour pressures determined is $\leq \pm 20$ Pa. The constants of the simplified Clausius–Clapeyron vapour pressure equation

$$\log(p/\mathrm{Pa}) = -\frac{A}{T/\mathrm{K}} + B \tag{2}$$

together with the mean enthalpy changes for the vaporization of liquid caffeine ΔH_v and the sublimation of solid α-caffeine $\overline{\Delta H_s}(\alpha)$ are complied in Table 2.

The vapour pressures over solid β-caffeine were also determined in the range 77–100°, in this case by the integral weight loss version of the Knudsen effusion

Table 2

Results of vapour pressure measurements

ϑ/°C	A/K^{-1}	B	$\overline{\Delta H_V}$ or $\overline{\Delta H_S}$/kJ · mole^{-1}	
236–251	3918±37	11.143±0.072	75.01±0.71	liquid caffeine, Hg-manometer
173–236	5223±28	13.697±0.057	99.99±0.54	α-caffeine, Hg-manometer
77–100	5781±35	15.031±0.113	110.68±0.67	β-caffeine, effusion measurements

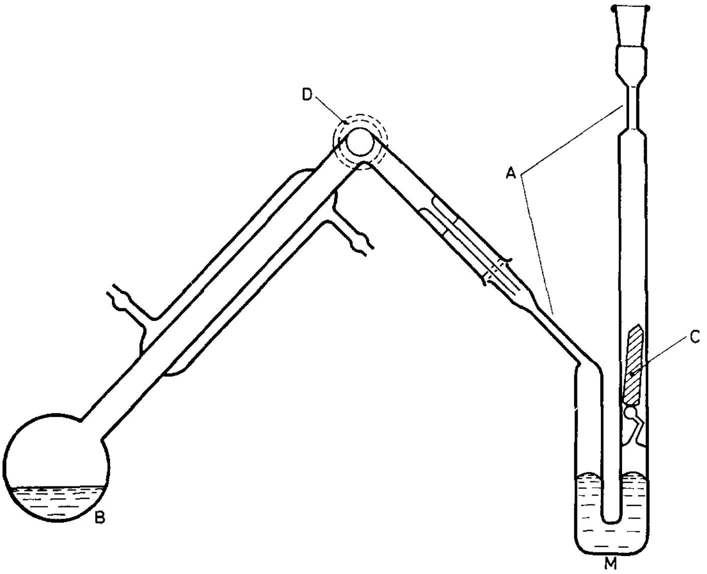

Fig. 3. Degasable mercury manometer. A: seal-off points, B: bulb for mercury degassing, C: break seal to substance tube, D: turnable joint to high vacuum line, M: mercury after degassing

method. The procedure and the apparatus used have been described in detail elsewhere [15, 16], so that a brief characterization may suffice here. Cylindrical pyrex glass effusion cells of cross-sectional area S were applied. At an inner height $h = 2.13\, r_c$ (r_c = inner cell radius) above the sample surface, the cells carried a molybdenum foil (13.0 ± 0.2 μm) with a centered circular effusion hole of area A. The effusion vapour was collected on a silvered condenser, automatically refilled with liquid nitrogen. Regulation of temperature was to ±0.03°; the uncertainty of the temperature was ±0.05° (IPTS–68). The Clausing correction factors W of the orifices ranged from 0.9624 to 0.9931, A was varied between

$0.8746 \cdot 10^{-3}$ and $29.201 \cdot 10^{-3}$ cm^2, and S between 1.431 and 1.6499 cm^2. The uncertainty of absolute weighing was ± 0.01 mg.

Two sets of measurements were performed. With constant effusion cell and orifice geometry, measurements of the apparent vapour pressure p' were made as a function of temperature and p' calculated by

$$p' = -\frac{\left(\frac{\partial m_e}{\partial t}\right)_T}{WA}\left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}}, \tag{3}$$

where $-\frac{\partial m_e}{\partial t}$ = rate of mass loss

W = Clausing factor (correction for finite orifice length)
A = area of effusion orifice
M = molar mass (194.19 g mole^{-1} for caffeine)
T = absolute temperature (T_{68}).

As with all dynamic vapour pressure measurements, and also with the effusion method, the measured apparent vapour pressure p' is lower than the saturated vapour pressure p, because the equilibrium between condensate and vapour is continuously disturbed. Unfortunately, this fact is neglected by many authors. The correlating equation between p' and p for effusion measurements using cells of the geometry described is [16]

$$p = \left(1 + \frac{WA}{\alpha\gamma S}\right)p'. \tag{4}$$

α = net evaporation coefficient
γ = a correction factor taking into account the roughness of the sample surface
S = cross-sectional area of cell.

The product $\alpha \cdot \gamma$ may be considered an effective evaporation coefficient. This was determined as follows. At a constant temperature p' was measured with various combinations of orifices and cells, thus changing $\frac{WA}{S}$. On plotting the observed p'

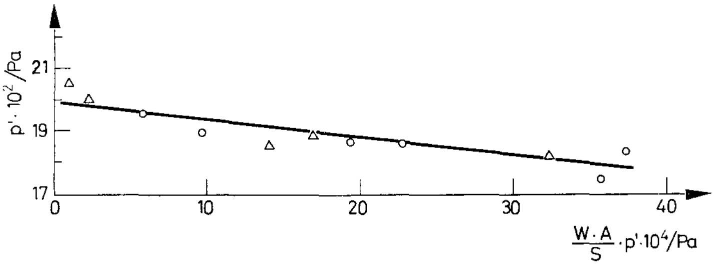

Fig. 4. Apparent pressure p' as a function of the effective ratio of orifice area WA to sample surface S at 94.29°

as a function of $\frac{WAp'}{S}$ (cf. Eq. 4), in the case of constant $\alpha \cdot \gamma$ we obtained this from the slope of the straight line fitted to the data by the method of least squares. Figure 4 shows the measurements for caffeine, yielding $\alpha_\gamma = 0.17 \pm 0.03$. Via this value, p was calculated from the measurements of p' at varied temperature by Eq. 4. The constants of the simple vapour pressure equation, Eq. 2, together with the resulting $\overline{\Delta H_s}(\beta)$, may be found in Table 2.

From the measured vapour pressures of β-caffeine, $\overline{\Delta H_s}(\alpha) = \overline{\Delta H_s}(\beta) - \Delta H_t^\circ$ and the measured transition temperature of $\vartheta_t = 141°$, the vapour pressures of α-caffeine, which is metastable below 141°, could be calculated. A Rankine–Dupré vapour pressure equation was then fitted by the method of least squares to these data and the static vapour pressure measurements made on α-caffeine at higher temperature. The resulting equation is

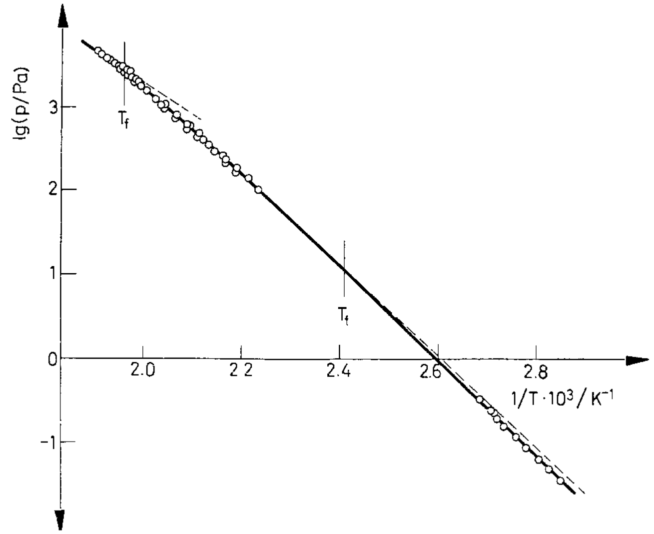

Fig. 5. Vapour pressure of solid and liquid caffeine, see text for details (T_t = temperature of transition, T_f = temperature of fusion)

$$\log(p/\text{Pa}) = -\frac{6632}{T/\text{K}} - 6.7058 \log(T/\text{K}) + 34.631 \tag{5}$$

The vapour pressure measurements made, the equation of type (2) for liquid and solid β-caffeine, and Eq. 5 for solid α-caffeine are shown in Fig. 5. The resulting enthalpy of fusion, as calculated from the vapour pressure equations at their intersection, i.e. the triple point, is included in Table 1. This value is close to the calorimetric result, and illustrates the consistency of the data obtained.

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RÉSUMÉ — La caffĕine présente une forme basse température (β) et haute température (α). Les données suivantes ont été déterminées par ATD quantitative : température de transformation 141±2°, enthalpie de transition 4.03 ± 0.1 kJ · mole^{-1}, enthalpie de fusion 21.6 ± 0.5 kJ · · mole^{-1}, chaleur spécifique molaire

$\vartheta/°C$	100 (β)	100 (α)	150 (α)	200 (α)
$C_p^\circ/J \cdot K^{-1} \cdot mole^{-1}$	271 ± 9	287 ± 10	309 ± 11	338 ± 10,

en bon accord avec les données obtenues par calorimétrie à chute. Les mesures sous pression de vapeur statique effectuées sur la caffĕine liquide et solide (α) ainsi que les mesures d'effusion sur la caffĕine liquide et solide (α) ainsi que les mesures d'effusion sur la caffĕine solide (β) ont donné pour les constantes de l'équation $\lg(p/\mathrm{Pa}) = -A/T + B$:

$A = 3918\pm37;\ 5223\pm28;\ 5781\pm35\ \mathrm{K}^{-1}$
$B = 11.143\pm0.072;\ 13.697\pm0.057;\ 15.031\pm0.113.$

Le coefficient d'évaporation de la caffĕine β est 0.17 ± 0.03.

ZUSAMMENFASSUNG — Es wurde festgestellt, daß Caffein bei niedrigen Temperaturen eine β- und bei hohen Temperaturen eine α-Modifikation besitzt. Durch quantitative DTA wurden folgende Angaben bestimmt: Umwandlungstemperatur 141 ± 2 °C, Umwandlungsenthalpie 4.03 ± 0.1 kJ $\cdot$ Mol^{-1}, Schmelzenthalpie 21.6 ± 0.5 kJ $\cdot$ Mol^{-1}, molare Wärmekapazität

ϑ/°C	100 (β)	100 (α)	150 (α)	200 (α)
C_p°/J $\cdot$ K^{-1} $\cdot$ Mol^{-1}	271 ± 9	287 ± 10	309 ± 11	338 ± 10

Sie stimmten gut mit den tropfkalorimetrischen Daten überein. Statische Dampfdruckmessungen an flüssigem und festem α- und Effusionsmessungen an festem β-Caffein ergaben für die Konstanten der Gleichung $\lg(p/\mathrm{Pa}) = -A/T + B$:

$A = 3918 \pm 37;\ 5223 \pm 28;\ 5781 \pm 35\ \mathrm{K}^{-1}$
$B = 11.143 \pm 0.072;\ 13.697 \pm 0.057;\ 15.031 \pm 0.113.$

Der Verdampfungskoeffizient von β-Caffein beträgt 0.17 ± 0.03.

Резюме — Было найдено, что кофеин существует в низкотемпературной β- и высокотемпературной α- модификации. С помощью количественного ДТА были определены такие параметры как температура превращения $141 + 2$ °С, энтальпия перехода 4.03 ± 0.1 кдж $\cdot$ $\cdot$ моль$^{-1}$, энтальпия плавления 21.6 ± 0.5 кдж$\cdot$моль$^{-1}$ молярная теплоемкость

ϑ/°C	100(β)	100 (α)	150 (α)	200 (α)
C_p°/Дж$\cdot$K^{-1}$\cdot$моль$^{-1}$	271 ± 9	287 ± 10	309 ± 11	338 ± 10

которые хорошо согласуются с данными капельной калориметрии. Измерения паров жидкого и твердого, а также эффузионные измерения твердого β-кофеина позволили определить константы уравнения $\lg(p/\text{Па}) = -A/T + B$:

$A = 3918 \pm 37;\ 5223 \pm 28;\ 5781 \pm 35\ \mathrm{K}^{-1}$
$B = 11.143 \pm 0.072;\ 13.697 \pm 0.057;\ 15.031 \pm 0.113.$

Коэффициент испарения β-кофеина равен 0.17 ± 0.03.