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Low-temperature heat-capacity and standard molar enthalpy of formation of copper L-threonate hydrate $Cu(C_4H_6O_5)\cdot 0.5H_2O(s)$

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Abstract

The solid copper L-threonate hydrate, $Cu(C_4H_6O_5)\cdot 0.5H_2O$, was synthesized by the reaction of L-threonic acid with copper dihydrocarbonate and characterized by means of chemical and elemental analyses, IR and TG-DTG. Low-temperature heat-capacity of the title compound has been precisely measured with a small sample precise automated adiabatic calorimeter over the temperature range from 77 to 390 K. An obvious process of the dehydration occurred in the temperature range between 353 and 370 K. The peak temperature of the dehydration of the compound has been observed to be 369.304 ± 0.208 K by means of the heat-capacity measurements. The molar enthalpy, $\Delta_d H_m$, of the dehydration of the resulting compound was of $16.490 \pm 0.063\ \mathrm{kJ\,mol^{-1}}$. The experimental molar heat capacities of the solid from 77 to 353 K and the solid from 370 to 390 K have been, respectively, fitted to tow polynomial equations with the reduced temperatures by least square method. The constant-volume energy of combustion of the compound, $\Delta_c U_m$, has been determined as being $-1616.15 \pm 0.72\ \mathrm{kJ\,mol^{-1}}$ by an RBC-II precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ$, has been calculated to be $-1114.76 \pm 0.81\ \mathrm{kJ\,mol^{-1}}$ from the combination of the data of standard molar enthalpy of combustion of the compound with other auxiliary thermodynamic quantities.

Keywords: $Cu(C_4H_6O_5)\cdot 0.5H_2O(s)$; Low-temperature heat-capacity; Adiabatic calorimetry; Rotating-bomb combustion calorimetry; Standard molar enthalpy of formation

1. Introduction

L-Threonic acid is an important carrier of many metal ions necessary for the life, which is intimately concerned with the biological metabolism. The compounds derived from L-threonic acid and various biological metal elements facilitate these metal ions combination with amino acids or proteins in the biological body and improve the efficiencies of the absorption and utilization of these metal ions in the biological body [1]. Copper is an essential trace element required for the correct functioning of human cells, due to its implication as a catalytic component in many important enzymes [2,3]. Reports abound in the literature concerning the active role of copper complexes in the control of inflammatory diseases [4]. As a potentially chemical and biological reagent, the complex of copper L-threonate encourages our interest.

In the present work, copper L-threonate hydrate, $Cu(C_4H_6O_5)\cdot 0.5H_2O(s)$, was synthesized through treatment of L-threonic acid with copper dihydrocarbonate and characterized by means of IR, TG-DTG, chemical and elemental analyses. It is more important that the thermodynamic properties of the compound have been deeply investigated by adiabatic calorimetry and combustion calorimetry.

2. Experimental

2.1. Reagents

L-Ascorbic acid, calcium carbonate, absolutely anhydrous ethanol, hydrogen peroxide (30 mass%), and copper dihydrocarbonate were of analytical grade purchased from Xi'an Chemical Reagent Company.

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2.2. Apparatus and analytical methods

C and H contents were carried out by an instrument of Vario EL III CHNOS of German. IR spectra were obtained with samples in KBr matrix for the title complex and ligand on A BEQ UZNDX-550 series FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. TG-DTG tests were performed in a Perkin-Elmer thermobalance under dynamic atmosphere of high purity N_2 (mass fraction 0.99999) with flow rate of 60 $cm^3\,min^{-1}$ and a heating rate of 10 $K\,min^{-1}$. The phase structure of the solid compound was identified by a Rigua D/max-IIIC X-ray diffractometer using Cu Kα radiation. The purity of the compound was attested by an HP-1100 type high-performance liquid chromatography analyzer, and the solvent was water, the rinsing reagent was ethanol and the column was contra-phase carbon-18.

2.3. Adiabatic calorimetry

A precision automatic adiabatic calorimeter established by Tan and others was used to measure the heat-capacity of the compound, the structure and principle of which have been described in detail elsewhere [5–7]. Its working temperature range was from the low temperature of 77 K, cooled by liquid nitrogen, to the high temperature of 390 K. Prior to the heat-capacity measurement of the sample, the molar heat capacities of α-Al_2O_3, the standard reference material, were measured to verify the reliability of the adiabatic calorimeter in the temperature range of 77–390 K, indicating that the relative deviation of calibration data was within ±0.3% [8]. The heat-capacity measurements were conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate was in the range of 0.1–0.4 $K\,min^{-1}$, the temperature increment of the experimental point was of the range of 1–4 K, the heating duration was 10 min and the temperature drift rates of the sample cell measured in an equilibrium period were kept within 10^{-3} to 10^{-4} $K\,min^{-1}$.

2.4. Rotating-bomb combustion calorimetry

The constant-volume combustion energy of the compound was measured by an RBC-type II precision rotary-bomb combustion calorimeter. The structure and principle of the calorimeter have been described in detail also elsewhere [9]. The temperature of the thermostatic water in the bath was automatically maintained at 298.15 ± 0.001 K by means of a precise thermostat. The temperature gauge from the digital indicator with integrated circuit was used to measure the temperature of the calorimetric tube. The bicyclic structure of the crucible support in the oxygen bomb was constructed so that the bomb could make a compound rotate about an axis perpendicular to the bomb axis (end-over-end rotation) and about the bomb axis (axial rotation) at the same time, which assured the complete combustion of the compound.

The temperature rise was corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correction value of the heat exchange was calculated according to Ref. [10].

The analyses of the final gas of the combustion reaction were referred to Ref. [9]. The amount of CO_2(g) was determined through the weight increment of the tube containing alkali asbestos after absorbing the carbon dioxide.

The total amount of acid was obtained through titration with a standard solution of NaOH. The identity of the final solid product was checked by the chemical analysis and XRD. The analyses of the combustion products indicated that the compound was combusted to the CO_2(g), H_2O(l) and CuO(s) under the excessive oxygen. The amount of NO_x and CO in the final gas phase may be neglected.

The energy equivalent of the RBC-type II calorimeter was determined from six combustion experiments to use approximate 0.8 g of benzoic acid with a certified massic energy of combustion, $\Delta_c U = -26434 \pm 3\,J\,g^{-1}$, under the same experimental conditions to be of $\varepsilon_{calor} = 18007.71 \pm 8.42\,J\,K^{-1}$.

2.5. Synthesis, purification and characterization of the sample

0.01 mol of solid calcium L-threonate, being prepared by a procedure given in Refs. [11,12], was dissolved in 200 cm^3 of distilled water, to which a solution containing 0.01 mol of oxalic acid was added. With stirring for 1 h, a great amount of white precipitation was produced in the mixed solution. The precipitation was filtered, and the equimolar copper dihydrocarbonate was added to the filter liquor under the mild heating. The reaction mixture was stirred for 3 h until many bubbles appeared. Following the procedures of cooling, filtration and condensation under the reduced pressure, addition of 100 cm^3 of anhydrous alcohol to the condensed filter liquor leaded to white precipitation. The precipitation was washed for three times with a little amount of anhydrous alcohol. At last, the final product was dried under the vacuum until the weight of the sample kept constant.

3. Results and discussion

3.1. Characterization of the compound

The chemically and elementally analytical results of the title compound are as follows: w (calcd): Cu 30.75%, C 23.25%, H 3.41%; w (found): Cu 30.68%, C 23.28%, H 3.52%, which is identified with the formula of $Cu(C_4H_6O_5)\cdot 0.5H_2O$. The purity of the sample was determined to be higher than 0.9995 by HPLC. The substance can be easily dissolved into distilled water, but faintly into methanol and cannot be dissolved into ethyl alcohol.

IR spectra of the title compound and L-threonic acid are shown in Fig. 1, and Vibration characteristic absorptions of main groups are listed in Table 1 [13].

It can be seen from Table 1 that, as for the threonic acid, the absorption peak of OH stretching vibration, $\gamma_{O\text{–}H}$, obviously shifted to the low wave number, and a wide and strong absorption peak appeared in 3400–3200 cm^{-1}, owing to strong association between these poly-hydroxide compounds. The hydrogen bonds formed between hydroxyl and carbonyl decreases the strength

Table 1
Data of IR absorption of main groups of L-threonic acid and hydrate copper L-threonate (γ, cm^{-1})

Compounds	$\nu_{O–H}$	$\nu_{C–H}$	$\nu_{C=O}$	$\nu_{as(COO–)}$	$\nu_{s(COO–)}$	$\nu_{C–O}$
L-Threonic acid	3366	2928	1740	–	–	1204, 1092, 1131, 1011
Hydrated copper L-threonate	3435	2939	–	1618	1420, 1315	1123, 1077

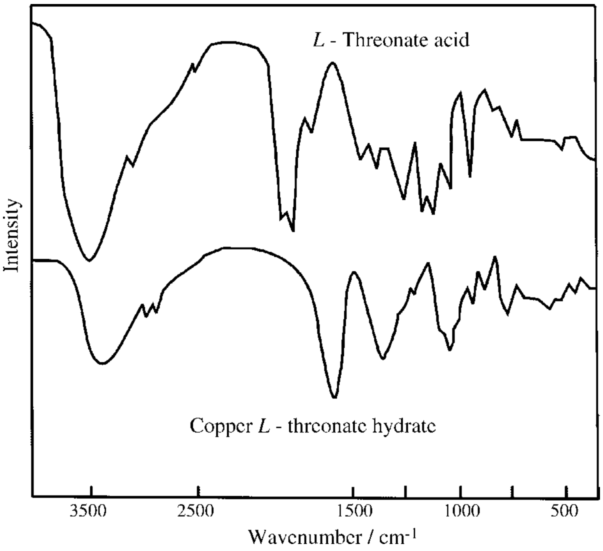

Fig. 1. IR spectra of the compound $Cu(C_4H_6O_5)\cdot 0.5H_2O$ and L-threonic acid.

of double bond of the carbonyl in molecule, as a result, the absorption peak of the C=O stretching vibration, $\gamma_{C=O}$, shifts to the low wave number, 1740 cm^{-1}. The absorption peak of OH stretching vibration, $\gamma_{O–H}$, based on the association of its two molecules and the formation of the hydrogen bond between hydroxyl and carbonyl moves from 3500 cm^{-1} to low wave number, a wide peak appeared in 3200–2500 cm^{-1}. As for the novel compound, its carbonyl possessed the distinctly different characteristic absorption peaks relative to that of the threonic acid, showing that oxygen atom of the carbonyl binds with the copper ion The characteristic peaks of 1400 and 1618 cm^{-1} are assigned as those of the symmetrical and the asymmetrical stretching vibrations, $\nu_{s(COO–)}$ and $\nu_{as(COO–)}$, respectively. A wide and scattered abortion at 3435 cm^{-1} is known as the display of the crystallization water involving in the title compound.

TG-DTG technique was applied to determine the stability of the compound. It can be seen from the TG-DTG curves shown in Fig. 2 that two obvious mass-loss processes take place with the temperature rising. The first mass-loss took place in the temperature range of 60–121 °C and the mass-loss percentage is 4.97%, which is in well agreement with the percent content (4.44%) of water in the new compound. The second mass-loss process occurs over the temperature region of 121–586 °C and the mass-loss percentage is 51.09%, which agrees with the theoretical mass-loss (51.69%) when the remains of the first process is further decomposed to CuO. The intermediate product was identified as $Cu(C_4H_6O_5)$ by IR spectrum and final product as CuO by XRD technique.

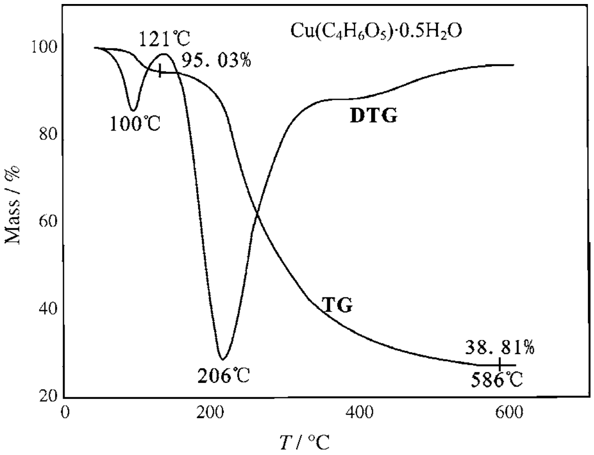

Fig. 2. TG-DTG curves of the compound $Cu(C_4H_6O_5)\cdot 0.5H_2O$.

Thermal decomposition process of the compound was derived from the results of TG-DTG analysis as follows:

$$Cu(C_4H_6O_5)\cdot 0.5H_2O \xrightarrow[95.03\%(95.66\%)]{60–100–121\,°C} Cu(C_4H_6O_5) + 0.5H_2O \xrightarrow[38.81\%(38.31\%)]{121–206–586\,°C} CuO + H_2O + CO_2 \quad (1)$$

3.2. Low-temperature heat-capacity

All heat-capacity experimental results (see Supplementary material) plotted in Fig. 3, showed that two stable phases,

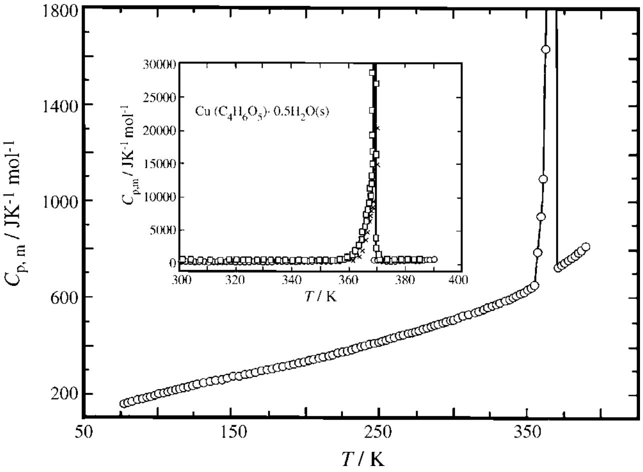

Fig. 3. The experimental molar heat-capacity curve of the solid compound $Cu(C_4H_6O_5)\cdot 0.5H_2O$ (M = 206.6491 g mol^{-1}) with the temperature (K). In which (×) represses the first series of heat-capacity measurements; (△) represses the second series of heat-capacity measurements; (○) represses the third series of heat-capacity measurements.

Table 2
The results of thermal decomposition of obtained from three groups of heat-capacity measurements for the compound $Cu(C_4H_6O_5)\cdot 0.5H_2O(s)$

Thermodynamic properties	x_1	x_2	x_3	$(\bar{x} \pm \sigma_a)$[a]
T_d (K)	369.232	368.986	369.694	369.304 ± 0.208
$\Delta_d H_m$ (kJ mol^{-1})	16.379	16.598	16.493	16.490 ± 0.063

[a] $\sigma_a = \sqrt{\sum_{i=1}^{3}(x_i - \bar{x})^2/n(n-1)}$ in which n is the experimental number; x_i, a single value in a set of heat-capacity measurements; $\bar{x}$, the mean value of a set of measurement results.

solid I from 77 to 353 K and solid II from 370 to 390 K, occur in the heat-capacity curve over the temperature range of $77\,\text{K} \le T \le 390\,\text{K}$, the temperature region of the dehydration from the solid I to the solid II was from 353 to 370 K. The experimental values of the heat capacities for two stable phases have been fitted to polynomial equations of the heat capacities against the reduced temperature by means of the least square method.

For the solid I:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 356.80837 + 215.44534x + 61.8843x^2 - 0.71731x^3 - 59.71806x^4 + 26.37058x^5 + 37.10181x^6 \quad (2)$$

where x is the reduced temperature, $x = (T - 215)/138$. The above equation is valid in the temperature range from 77 to 353 K, with an uncertainty of ±0.25%.

For the solid II:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 760.74905 + 42.78432x + 2.94078x^2 + 3.79281x^3 + 0.06558x^4 \quad (3)$$

where $x = (T - 380)/10$. The above equation is useful in the temperature range from 382 to 395 K, with an uncertainty of ±0.20%.

3.2.1. Peak temperature and molar enthalpy of the dehydration process

It is found from the heat-capacity curve that the second endothermic peak appeared in the temperature range of 382–395 K, which was covered in the temperature region of 60–121 °C corresponding to the dehydration of the compound, as obtained in TG-DTG curve. Three series of heat-capacity experiments in the thermal decomposition region of the compound were carried, indicating that the reversibility and repeatability of the thermal decomposition are verified.

The dehydration temperature T_d of the sample was determined to be 369.304 ± 0.208 K from the peak temperature of thermal decomposition based on the heat-capacity data. The difference between the dehydration temperatures obtained from the heat-capacity measurements and the TG-DTG analysis was mainly attributed to the absorption water on the surface of the sample in the TG-DTG analysis. The molar enthalpy of the dehydration, $\Delta_d H_m$, of the substance was determined following the method described in Ref. [7].

The results of T_d and $\Delta_d H_m$ of the sample obtained from a set of three-repeated heat-capacity measurements are listed in Table 2.

3.3. Constant-volume combustion energy, standard molar enthalpy of combustion and standard molar enthalpy of formation

The method for determining the constant-volume combustion energy of the sample is the same as that used in the calibration of the calorimeter with benzoic acid. The constant-volume combustion energy of the sample can be calculated according to Refs. [9,10].

The measured results of the constant-volume combustion energy of the sample are indicated in Table 3.

The standard molar enthalpy of combustion of the sample, $\Delta_c H_m^\circ$, refers to the combustion enthalpy change of the following reaction at 298.15 K and 100 kPa:

$$Cu(C_4H_6O_5)\cdot \tfrac{1}{2}H_2O(s) + \tfrac{7}{2}O_2(g) = CuO(s) + 4CO_2(g) + \tfrac{7}{2}H_2O(l) \quad (4)$$

The standard molar enthalpies of combustion of the sample can be derived from the constant-volume combustion energy by

Table 3
The experimental results of constant-volume combustion energy for the compound $Cu(C_4H_6O_5)\cdot 0.5H_2O(s)$ at 298.15 K

No.	Mass of sample, a (g)	Corrected heat of ignition wire, q_c (J)	Corrected heat of nitric acid, q_N (J)	Corrected temperature rise, $\Delta_c T$ (K)	Combustion energy of sample, $-\Delta_c U$ (J g^{-1})
1	1.23560	11.70	19.40	0.5388	7824.28
2	1.20183	10.80	18.87	0.5231	7810.17
3	1.24500	11.70	19.55	0.5434	7831.60
4	1.30056	9.00	20.42	0.5663	7815.39
5	1.25434	12.60	19.70	0.5464	7815.50
6	1.20685	11.70	18.95	0.5266	7829.08
Mean					7821.00 ± 3.50

Eqs. (5) and (6):

$$\Delta_c H_m^\circ = \Delta_c U_m^\circ + \Delta n RT \tag{5}$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \tag{6}$$

where $\sum n_i$ was the total amount (in mol) of gas present as products or as reactants. The calculated standard molar enthalpy of combustion of the sample, $\Delta_c H_m^\circ$, is $-1616.77 \pm 0.72\,\text{kJ mol}^{-1}$.

The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ$, is calculated by a designed Hess' thermochemical cycle according to reaction (7) as follows:

$$\begin{aligned}&\Delta_f H_m^\circ[\text{Cu}(\text{C}_4\text{H}_6\text{O}_5)\cdot \tfrac{1}{2}\text{H}_2\text{O, s}]\\ &\quad= [\Delta_f H_m^\circ(\text{CuO, s}) + 4\Delta H_m^\circ(\text{CO}_2\text{, s}) + \tfrac{7}{2}\Delta H_m^\circ(\text{H}_2\text{O, l})]\\ &\qquad - \Delta_c H_m^\circ[\text{Cu}(\text{C}_4\text{H}_6\text{O}_5)\cdot \tfrac{1}{2}\text{H}_2\text{O}]\end{aligned} \tag{7}$$

In Eq. (7), the standard molar enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and $CuO(s)$, recommended by CODATA [14], $\Delta_f H_m^\circ(\text{CuO, s}) = -155.23\,\text{kJ mol}^{-1}$, $\Delta_f H_m^\circ(\text{CO}_2\text{, g}) = -393.51 \pm 0.13\,\text{kJ mol}^{-1}$ and $\Delta_f H_m^\circ(\text{H}_2\text{O, l}) = -285.83 \pm 0.04\,\text{kJ mol}^{-1}$, are employed in the calculation of $\Delta_f H_m^\circ[\text{Cu}(\text{C}_4\text{H}_6\text{O}_5)\cdot 0.5\text{H}_2\text{O, s}]$. The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ[\text{Cu}(\text{C}_4\text{H}_6\text{O}_5)\cdot 0.5\text{H}_2\text{O, s}]$, can be derived based on these values and the standard molar enthalpy of combustion of the substance to be $-1114.76 \pm 0.81\,\text{kJ mol}^{-1}$.

4. Conclusions

A biologically active compound, $Cu(C_4H_6O_5)\cdot 0.5H_2O$, was synthesized and characterized by IR and TG-DTG techniques. Low-temperature heat-capacity of L-threonate hydrate has been precisely measured with a small sample precise automated adiabatic calorimeter over the temperature range from 77 to 390 K. The constant-volume energy of combustion of the compound, $\Delta_c U_m$, has been determined as being $-1616.15 \pm 0.72\,\text{kJ mol}^{-1}$ by an RBC-II precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ$, has been calculated to be $-1114.76 \pm 0.81\,\text{kJ mol}^{-1}$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.12.008.

References

[1] X.D. Sun, X.C. Yin, S.R. Zhu, Chem. J. Chin. Univ. 19 (1998) 849 (in Chinese).

[2] J.P. Klinman, Chem. Rev. 96 (1996) 2541.

[3] E.I. Solomon, U.M. Sundaram, T.E. Machonkin, Chem. Rev. 96 (1996) 2563.

[4] D. Kovala-Demertzi, A. Galani, M.A. Demertzis, S. Skoulika, C. Kotoglou, J. Inorg. Biochem. 98 (2004) 358–364, and references therein.

[5] Z.C. Tan, G.Y. Sun, Y. Sun, J. Therm. Anal. 45 (1995) 59.

[6] Z.C. Tan, G.Y. Sun, Y.J. Song, L. Wang, J.R. Han, Y.S. Liu, Thermochim. Acta 252–253 (2000) 247.

[7] Z.C. Tan, L.X. Sun, S.H. Meng, L. Li, P. Yu, B.P. Liu, J.B. Zhang, J. Chem. Thermodyn. 34 (2002) 1417.

[8] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stand 87 (1982) 159.

[9] X.W. Yang, S.P. Chen, S.H.L. Gao, Instrum. Sci. Technol. 30 (2002) 311.

[10] M.W. Popov, Thermometry and Calorimetry, Moscow Univ. Publishing House, Moscow, 1954, p. 331 (in Russian).

[11] C.C. Wei, S. Debernardo, J.P. Tengi, J. Org. Chem. 50 (1985) 3462.

[12] H.S. Isbell, H.C. Frush, Carbohydr. Kes. 72 (1979) 301.

[13] Q.N. Dong, H. Guangpu, Infrared Spectra, 129, Chemical Industry Press, Beijing, 1979 (in Chinese).

[14] J.D. Cox, J. Chem. Thermodyn. 10 (1978) 903.