

ESTABLISHMENT OF THERMODYNAMIC PROPERTIES OF PURE SOLID SUBSTANCES BY THERMOMECHANICAL ANALYSIS

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Abstract

The combination of a DuPont 942 thermomechanical analyzer with a CBM computer allowed the establishment of thermodynamic properties such as isobars, isobaric volumetric expansions, isothermal compressibilities, and the equation of state $V = V(p, T)$ in a limited region of pVT space.

Keywords: thermomechanical analysis, thermodynamic properties

Introduction

Up-to-date computing techniques applied in conjunction with thermal analysis instrumentation allows the fast processing of data, which would otherwise be extremely time-consuming.

This paper reports on the combination of a DuPont 942 thermomechanical analyzer (TMA), commercially available software and a CBM Amiga computer. This combination permits the rapid acquisition of thermodynamic properties such as isobars, equations for isobaric volumetric expansion (α) and isothermal compressibility (κ), and the equation of state $V = V(p, T)$. Unfortunately, all these coefficients and equations are limited in their domain, especially in the pressure interval 70 to 110 kPa.

Experimental

Sample

The sample used, as an example, was glycine (447K46092)1 from E. Merck, Darmstadt (purity 99.7%, NH_4 0.02%, ninhydrin-positive, chloride 0.003%, heavy metals such as Pb, 0.001%).

After calibration of the TMA [1], 10 to 20 mg of sample was weighed, and tightly packed inside the quartz vial included with the dilatometer accessory kit.

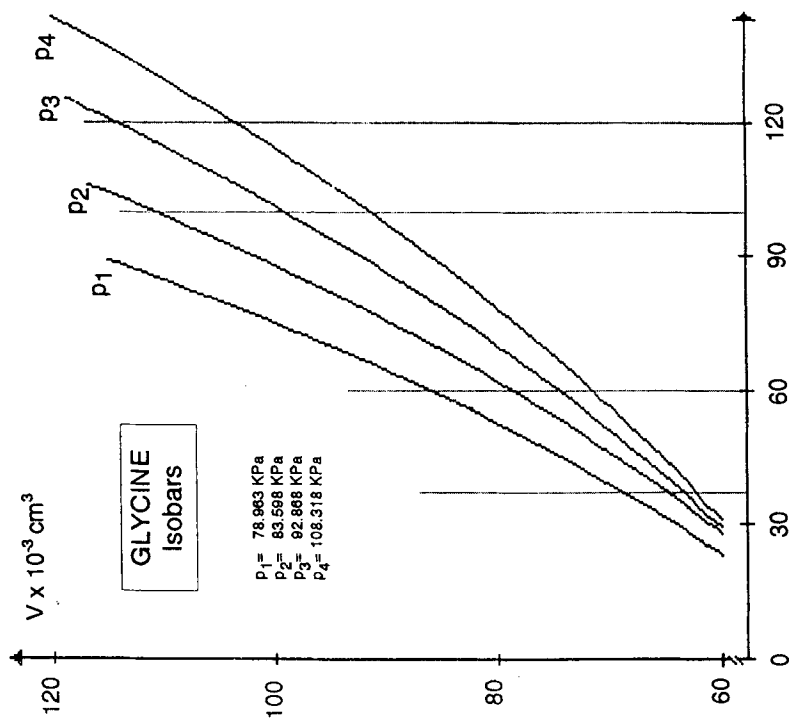


Fig. 2 Isobars

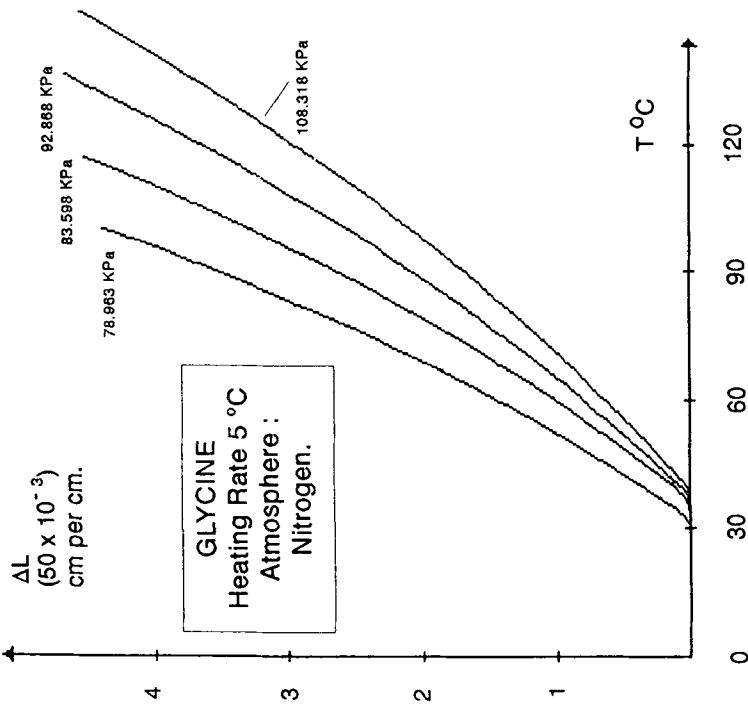


Fig. 1 ΔL as a function of sample temperature

Initially, a mass of 5 g was placed on the TMA weight tray, which exerted the initial mechanical pressure. For Universidad Metropolitana-Iztapalapa (Mexico City) coordinates (Lat. N: 19° 21' 22'', Long. WG: 99° 05' 30'' and 2280 meters of altitude), this initial absolute pressure was 78.963 kPa, with $g = 9.78698 \text{ ms}^{-2}$. A flow of nitrogen ($10 \text{ to } 20 \text{ cm}^3 \text{ min}^{-1}$) was introduced in the TMA module. The sample was then heated ($5 \text{ deg} \cdot \text{min}^{-1}$) up to 100°C , left for 1 h at this temperature for degassing and stabilization of the sample volume, next cooled until ambient temperature is reached, and then heated again up to 150°C .

Experimental results

The initial thermoanalytical curves which present ΔL (height variation) as a function of sample temperature (Fig. 1) are very well known [2–4] and are not discussed here.

The internal dimensions of the quartz vial are known and the initial volume, V_o , of the sample, under the starting conditions, was measured. From V_o and the calculated height increase (ΔL) of the sample with increasing temperature from the data in Fig. 1, the sample volume V_s , can be expressed as:

$$10^3 V_s / \text{cm}^3 = V_o + 80.5 \Delta L \quad (1)$$

The coefficient of ΔL is the area of the internal cylindrical vial base.

With the data thus obtained, the family of curves $V = V(T)$ at constant pressure (Fig. 2) is obtained.

So that Fig. 2 is clear, it does not present all the isobars (a minimum of ten). The intercepts of the dotted lines with the isobars provide coordinates for volume and pressure at constant temperature. With the data thus obtained from the isobars, the curves for α and κ are fitted (Figs 3 and 4).

Equations for α and κ were obtained (Table 1).

The degree of fit of the experimental data and the equations in Table 1 is presented in Table 2.

Equation of state in a limited region

There are two different approaches for the $V = V(p, T)$ evaluation:

a) Derivation of a general expression for $\kappa = \kappa(p, T)$ and $\alpha = \alpha(p, T)$ and their substitution in the classical equation:

$$dV = -\kappa(p, T)Vdp + \alpha(p, T)VdT \quad (2)$$

b) Fitting a surface over the family of isobars.

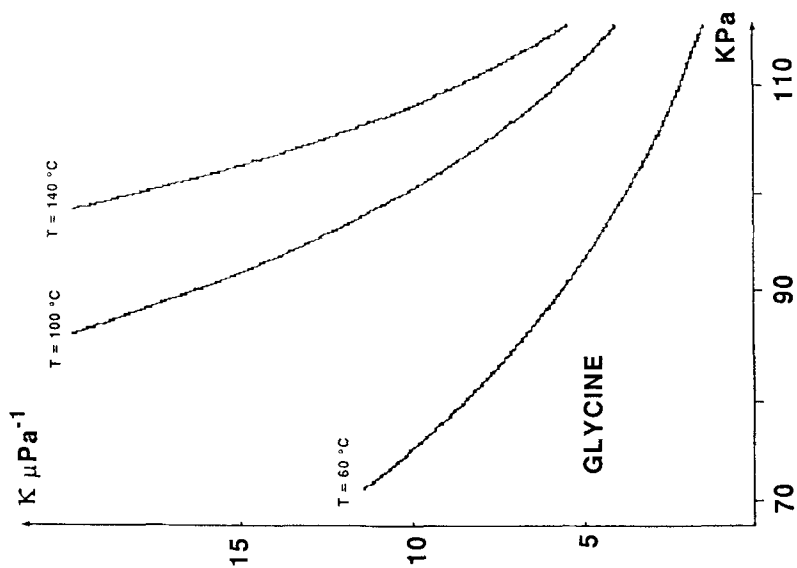


Fig. 4 Family of k_s

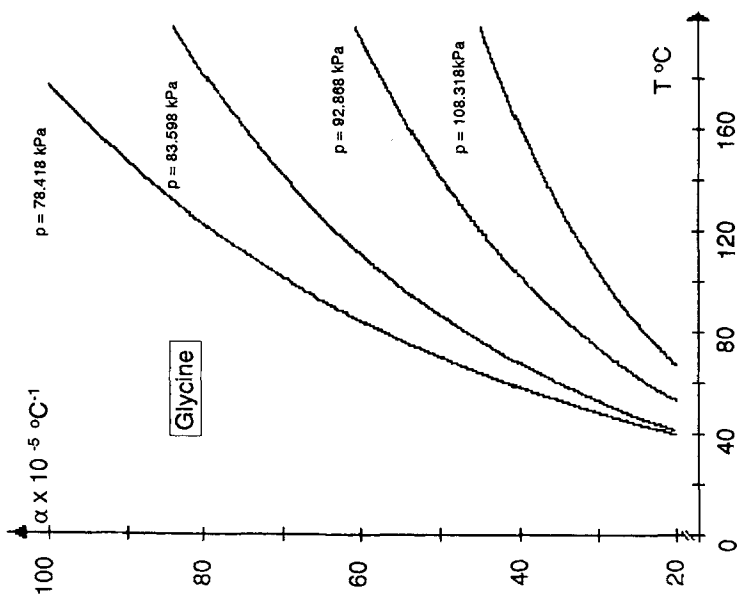


Fig. 3 Family of α_s

Table 1 Equations for α and κ

Glycine, equations for α_p	
$\alpha_{72.418}$	$\text{kPa} = -179.0009 + 53.896 (\ln T)$
$\alpha_{83.598}$	$\text{kPa} = -131.2588 + 40.6337 (\ln T)$
$\alpha_{92.868}$	$\text{kPa} = -102.5358 + 30.7084 (\ln T)$
$\alpha_{106.318}$	$\text{kPa} = -76.6248 + 22.9475 (\ln T)$
Glycine, equations for κ_T	
κ_{60}	$= 0.11254 \exp(-0.031568p)$
κ_{80}	$= 0.97299 \exp(-0.031568p)$
κ_{100}	$= 9.5894 \exp(-0.06559p)$

Units and Domain: Temperature in °C; pressure in kPa; T [30, 140]°C; p [70, 110]kPa

The first approach, although simple, leads to a differential equation whose integrating factor is, to say the least, not simple to evaluate. Thus, the second approach was used.

The equation of state $V = V(p, T)$ obtained for glycine is:

$$V = T(15.151476 + 7.268299 \ln p) \exp [0.032251 \exp (-0.015565p)] \quad (3)$$

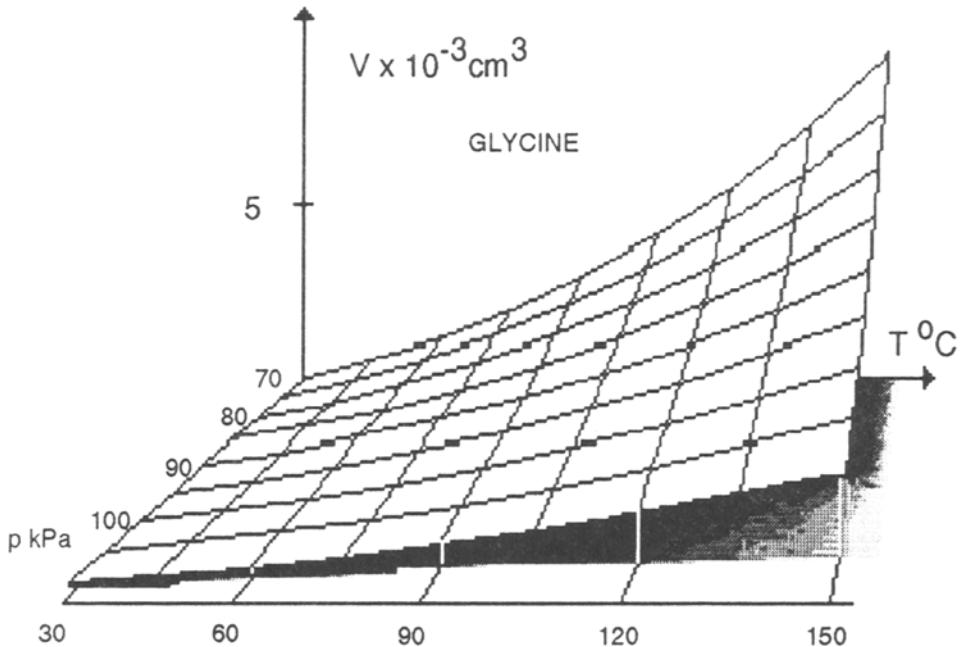


Fig. 5 $V = V(p, T)$ for glycine. Domain: pressure [70, 110] kPa and temperature [30, 140]°C

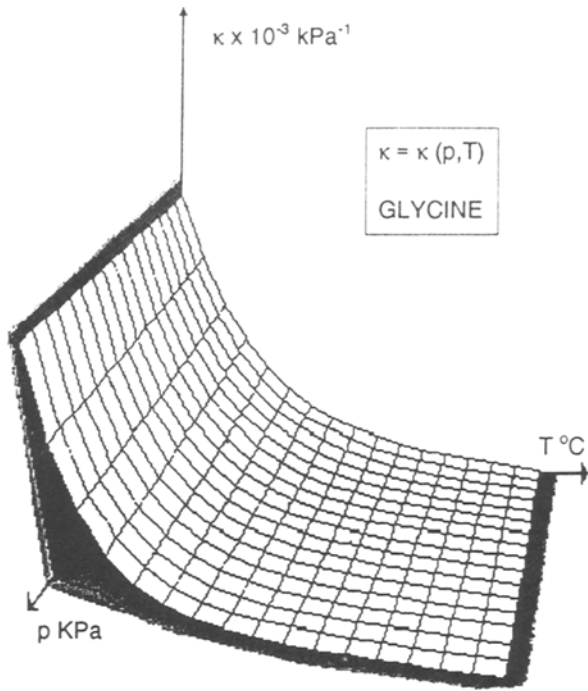


Fig. 6 $\kappa = \kappa(p, T)$ for glycine

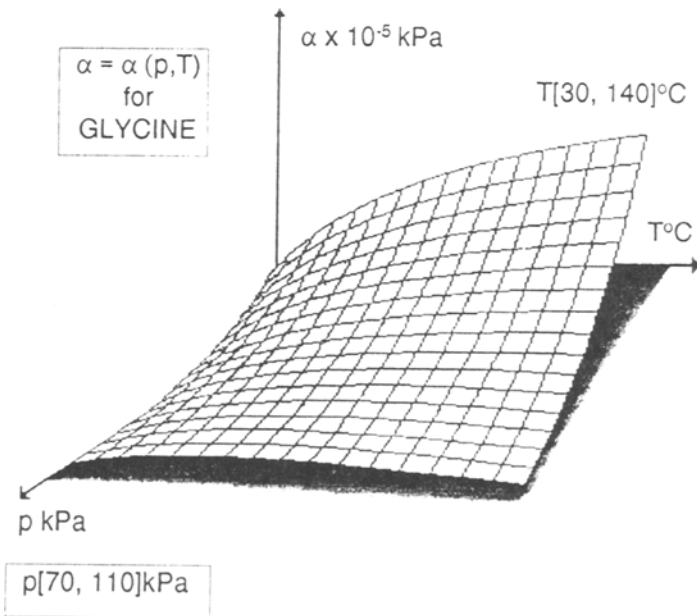


Fig. 7 $\alpha = \alpha(p, T)$ for glycine

Table 2 The degree of fit of the experimental data and the equations in Table 1

Glycine, values for α_p				
	α	α	α	α
T	77.418 kPa	83.598 kPa	93.868 kPa	108.318 kPa
$^{\circ}\text{C}$	$\times 10^{-5}, ^{\circ}\text{C}^{-1}$	$\times 10^{-5}, ^{\circ}\text{C}^{-1}$	$\times 10^{-5}, ^{\circ}\text{C}^{-1}$	$\times 10^{-5}, ^{\circ}\text{C}^{-1}$
Experimental calculated from equations in Table 1				
50	31.05342	27.68302	17.43984	13.06723
	31.84149	27.70117	17.59617	13.14635
85	61.00316	48.98932	33.90032	23.10000
	60.94023	49.00256	33.89091	23.32294
116	76.92867	59.98623	43.07294	32.45821
	77.19859	60.01971	43.43935	32.45821
140	88.37529	69.00000	49.00931	36.75214
	87.83386	69.53842	49.21413	36.77354
Glycine, values for κ_T				
p	$\kappa / 60^{\circ}\text{C}$	$\kappa / 100^{\circ}\text{C}$	$\kappa / 140^{\circ}\text{C}$	
kPa	$\times 10^{-3}\text{Pa}^{-1}$	$\times 10^{-3}\text{Pa}^{-1}$	$\times 10^{-3}\text{Pa}^{-1}$	
Experimental calculated from equations in Table 1				
77.418	0.00992	0.00266	0.0653	
	0.00977	0.00263	0.0598	
92.865	0.00586	0.00123	0.0197	
	0.00595	0.00128	0.0217	
100.0	0.00475	0.000907	0.0131	
	0.00479	0.000918	0.0136	
108.318	0.00362	0.000636	0.00872	
	0.00368	0.000623	0.00787	

This is valid only in the interval: pressure: [70, 110] kPa, temperature: [30, 140] $^{\circ}\text{C}$.

The differential of Eq. (3) satisfies the condition of being exact. The $V = V(p, T)$ surface is presented in Fig. 5.

Now, if Eq. (2) is applied to Eq. (3), $\kappa(p, T)$ and $\alpha(p, T)$ are easily obtained. Figures 6 and 7 present their graphs.

Software: For curve and equation-fitting: Math-Amation (Progressive Peripherals & Software, Inc.) and Descartes (Mindware – DTM Werbung GmbH). Function mapping: Math-Vision by Dough Houck (Seven Seas Software), the IEEE version and a 68881 math-coprocessor were used.

Conclusion

The combination of a DuPont TMA with a CBM Computer yields thermodynamic data quickly. The agreement between the experimental data and the fitted equations is good. The pressure interval is quite limited, which is due to the arrangement and dimensions of the TMA quartz sample probe. Several tests were made to increase the value of weights and obtain a greater applied pressure. Use of a laser to detect when bending of the quartz probe starts revealed that this occurs for 170 g.

References

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Zusammenfassung — Die Kombinierung eines DuPont 942 thermomechanischen Analysators mit einem CBM-Computer gestattet die Ermittlung thermodynamischer Eigenschaften, wie z.B. von Isobaren, isobaren volumetrischen Ausdehnungen, isothermen Kompressibilitäten und der Gleichung des Zustandes $V = V(p, T)$ in einem begrenzten Bereich des pVT -Raumes.