

SIMULTANEOUS EVALUATION OF P-v-T, ISOBARIC SPECIFIC HEAT AND JOULE – THOMSON COEFFICIENT MEASUREMENTS

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Abstract

A method is given in this paper that enables the simultaneous evaluation of P - v - T , isobaric specific heat and Joule – Thomson coefficient (J. T. C) measurements. It gives the ideal gas isobaric specific heat function and a semi-explicit $v = v(P, T)$ equation of state (E. O. S) as results. The results for the vapor phase of R227 are presented also.

Keywords: equation of state, isobaric specific heat, Joule – Thomson coefficient.

Introduction

Thermodynamic calculations in the gas phase need in addition to the ideal gas heat capacity an E. O. S. that is correct not only for a general description of the behavior but the derivatives of it are correct as well.

Therefore it is expedient to use measured specific heats and J. T. C.-s beside the P - v - T data for developing the E. O. S. The usage of the different kind quantities contributes to find the deficient measured values and it supports to find the regions where data miss.

Analysis

The enthalpy of the substances may be calculated in the following form if the independent variables are P and T :

$$h = h(P = 0, T_0) + \int_{T_0}^T c_p(P = 0, T') \cdot dT' + \int_0^P \left. \frac{\partial h(P', T')}{\partial P'} \right|_{T'=T} \cdot dP', \quad (1)$$

where

$$\left. \frac{\partial h}{\partial P} \right|_T = -T^2 \cdot \frac{\partial}{\partial T} \left[\frac{v(P, T)}{T} \right]. \quad (2)$$

Since the c_p and the J. T. C. measurements have been performed not with simultaneously measured densities, the E. O. S. has to be explicit in volume.

It follows from Eq. (2), that the part of the E. O. S. , which is linear in the temperature (which has the form $f(P) \cdot T$) has no effect on the enthalpy. This means that the E. O. S. may be developed from measured c_p and J. T. C. data only for a pressure domain where P - v - T data exist at least on one line.

The slope of the isothermal lines of a volume-expressed E. O. S. is very large in the critical region and it becomes infinite in the critical point; furthermore there is a discontinuity in these lines at the saturation line. To overcome the problems caused by these facts, it is expedient

- to exclude the critical region from the investigation,
- to give different E. O. S. for the vapor and for the liquid phase,
- to decompose the E. O. S. in two parts, into a basic function that is at least qualitatively correct and into a correcting part.

Mathematical Formulation

The specific heat function and the E. O. S. chosen for the calculation have the following form:

$$c_p(P = 0, T) = \sum_i A_i \cdot (T/T_x)^{B_i}, \quad (3)$$

$$v(P, T) = v_b(P, T) + \sum_j C_j \cdot (P/P_x)^{D_j} \cdot (T/T_x)^{E_j}, \quad (4)$$

$$\left(P + \frac{a}{v_b^n} \right) \cdot (v_b - b) = R \cdot T, \quad (5)$$

where $v_b(P, T)$ in Eq. (4) is the root of Dieterici's first equation (Eq. (5)) at the given P and T . Eq. (5) has been chosen for basic function because that is the simplest although a very inaccurate E. O. S. that gives both for the vapor and for the liquid phase not too bad densities.

The A_i , B_i , C_j , D_j and E_j constants were calculated by minimizing the deviations from the experimental data:

$$\sum (P \cdot v_{\text{calc}} - P \cdot v_{\text{exp}})^2 + \sum (\Delta h_{\text{calc}} - \Delta h_{\text{exp}})^2 + \sum (\Delta h_{\text{calc}} - 0)^2 = \min, \quad (6)$$

where the P - v - T measurements are taken into account in the first sum, the specific heat measurements in the second one and the J. T. C. measurements in the third.

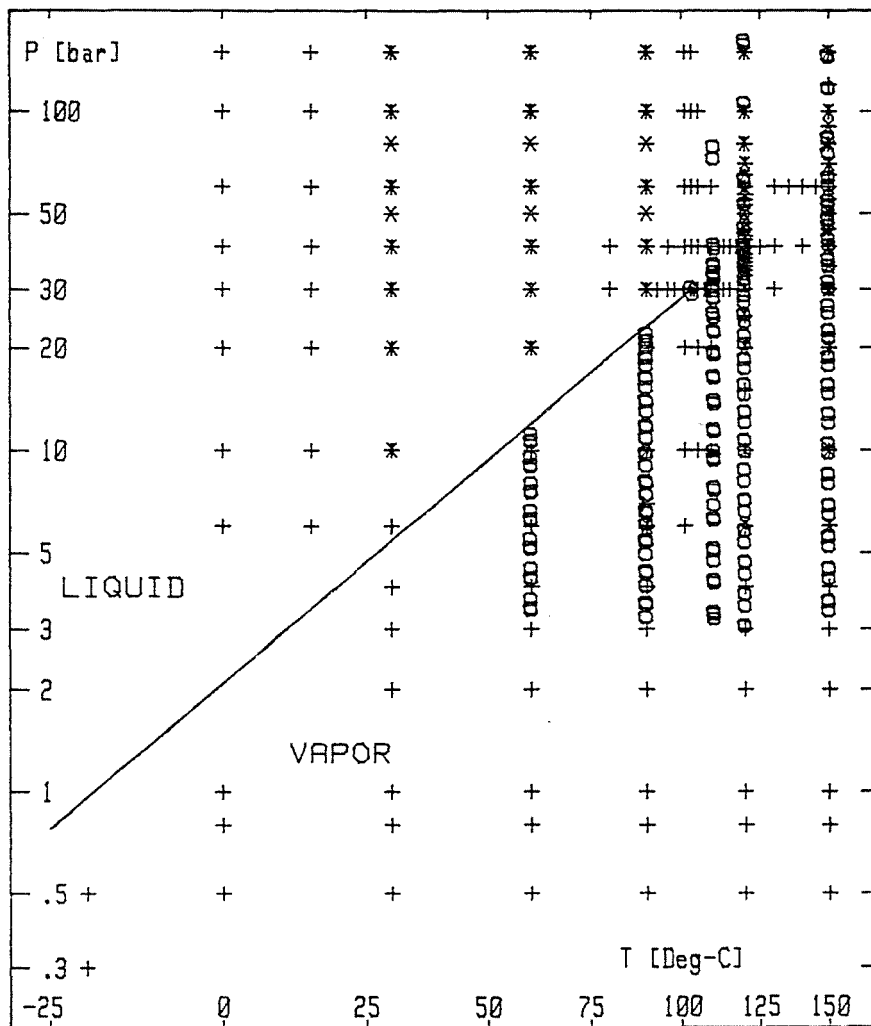


Fig. 1. Location of the measured data on the $P - T$ plane
 + : CP * : MU O : RHO

Not the c_p values and the J. T. C.-s were used for the calculation but the finite changes in the P , T , h quantities during these measurements, because both measured coefficients are not the true values, they are only mean values for finite temperature differences and pressure changes.

The B_i , D_j and E_j exponents were not taken for integers to reduce the items in Eq. (3) and Eq. (4).

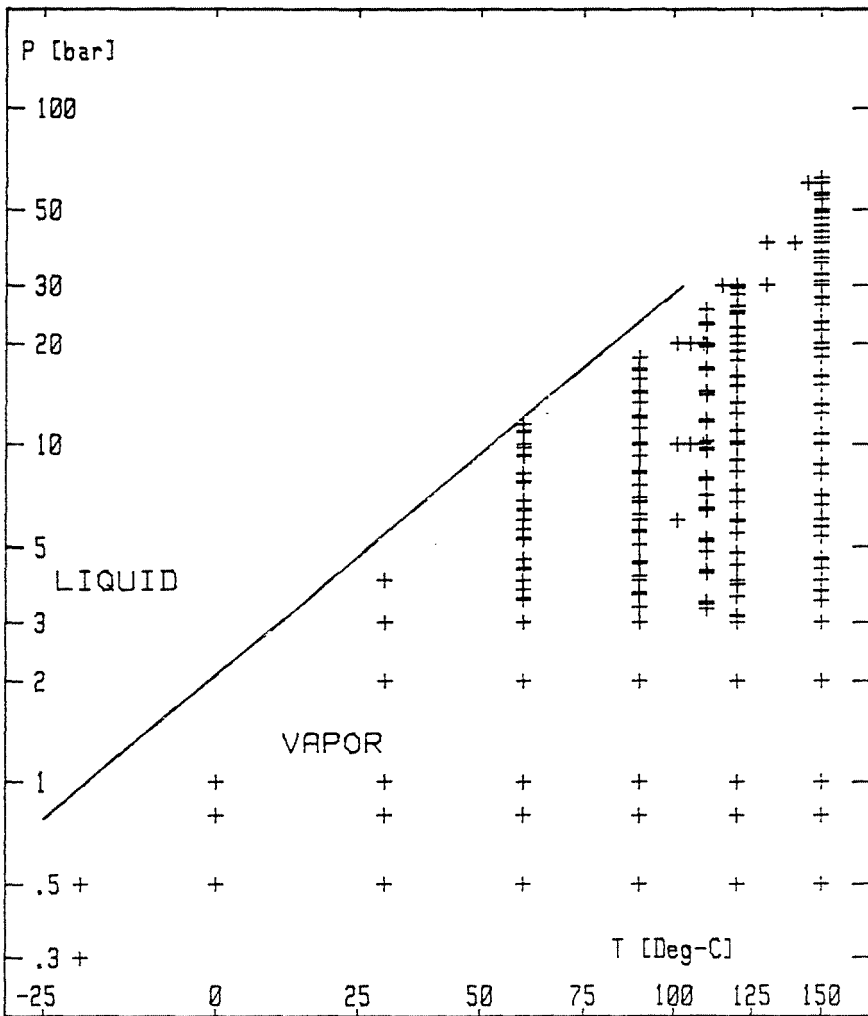


Fig. 2. Location of the used data on the $P - T$ plane

The calculation was stopped when the decrease of the expression on the left hand side of $Eq. (6)$ became slow.

Usage for R227

Measured $P-v-T$ data, J. T. C. data and isobaric specific heats were used for the development of the ideal gas specific heat function and the E. O. S.

The data were published elsewhere [1], [2]. The distribution of the measurements on the $P-T$ plane is shown in *Fig. 1*. 165 $P-v-T$ measurements, 66 specific heat data and 17 J. T. C. data were used for the evaluation. The distribution of the used measurements on the $P-T$ plane is shown in *Fig. 2*.

The average of the measured $P \cdot v$ products is 16000 J/kg, the average enthalpy change for the isobaric specific heat measurements is 5000 J/kg (the average temperature change is 5 K), the average pressure drop for the J. T. C. measurements is 3.7 bar (the enthalpy change is 0).

The constants in *Eq. (5)* are as follows: $R = 48.9$ J/kg, K, $a = 259.6822$, $b = 4.223594$ D-4m³/kg, $n = 1.6764858$, furthermore $P_x = 2.97$ E6 Pa, $T_x = 375.9$ K.

The calculated constants of *Eq. (3)* are as follows:

i	$B(i)$	$A(i)$
[-]	[-]	[J/kg,K]
1	0.72180	0.10966999E4
2	1.45510	-0.18003643E3
3	15.0000	-0.30525162E0

The calculated constants of *Eq. (4)* are as follows:

j	$D(j)$	$E(j)$	$C(j)$
[-]	[-]	[-]	[m ³ /kg]
1	0.0000	-0.1837	0.43455439E-1
2	0.1037	-0.2464	-0.61283797E-1
3	0.4168	-0.5108	0.22854952E-1
4	0.5607	-6.9887	-0.55742842E-3
5	1.5903	-9.5879	-0.42276712E-3
6	1.9382	-3.9241	-0.13803596E0
7	2.1844	-4.4612	0.10796829E1
8	2.2204	-4.5306	-0.94819510E0
9	5.2327	-8.6550	0.18654539E-1
10	6.2714	-10.1749	-0.30578918E-1
11	6.7880	-24.7299	-0.20262881E-1
12	6.9899	-24.3884	0.22071757E-1
13	7.0724	-10.9029	0.14468906E-1
14	7.2657	1.0000	-0.42871990E-4
15	9.4121	-29.2737	-0.82512463E-3
16	12.4952	-19.4747	-0.96372771E-3
17	15.0009	-21.1179	0.18264423E-2
18	15.5152	-21.2098	-0.16709381E-2
19	16.2080	-21.2089	0.31218494E-3

All the deviations from the measured data versus temperature are shown in *Fig. 3* and versus pressure in *Fig. 4*. The distribution of the deviations is shown in *Fig. 5*.

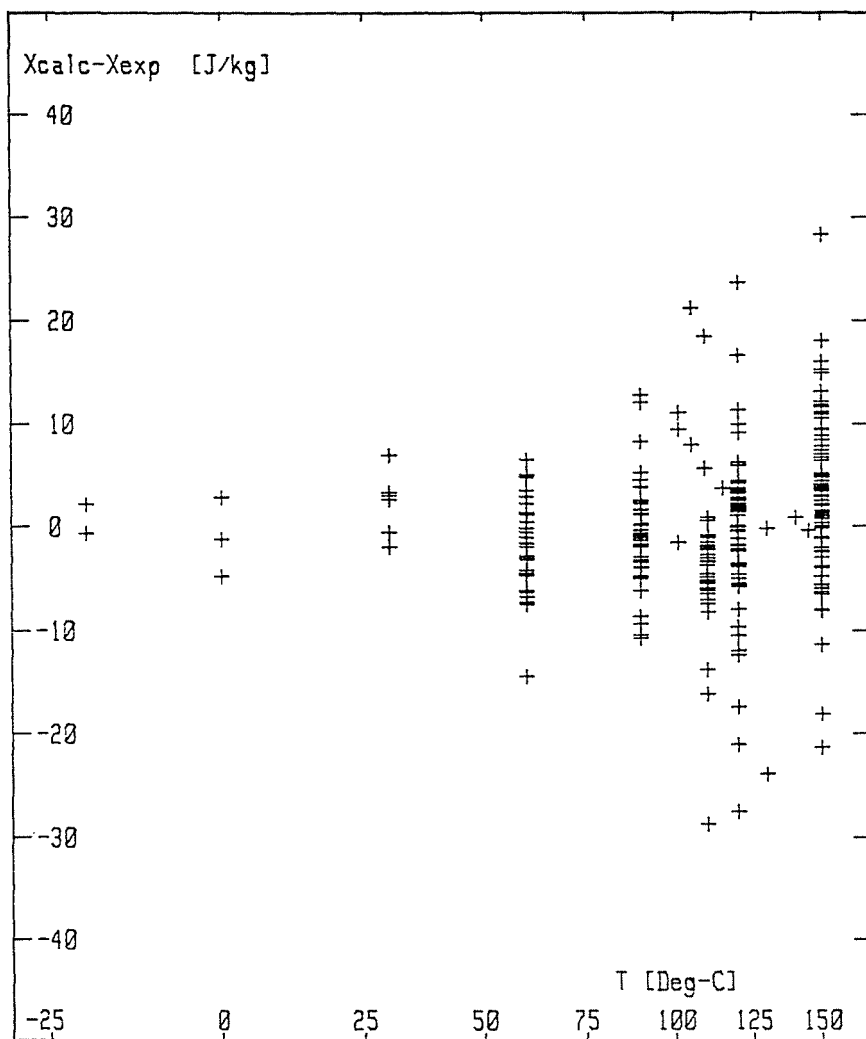


Fig. 3. Deviation from the experimental data at different temperatures

The measured density at 9.0006 bar and 120 °C was changed for the final calculation to 51.589 kg/m³ since the published value is obviously incorrect. The measured specific heat at 6 bar and 60 °C was excluded from the final calculation because it contradicts both the J. T. C. and the *P-v-T* measurements (the deviation may be cca 13.5 J/kg, K).

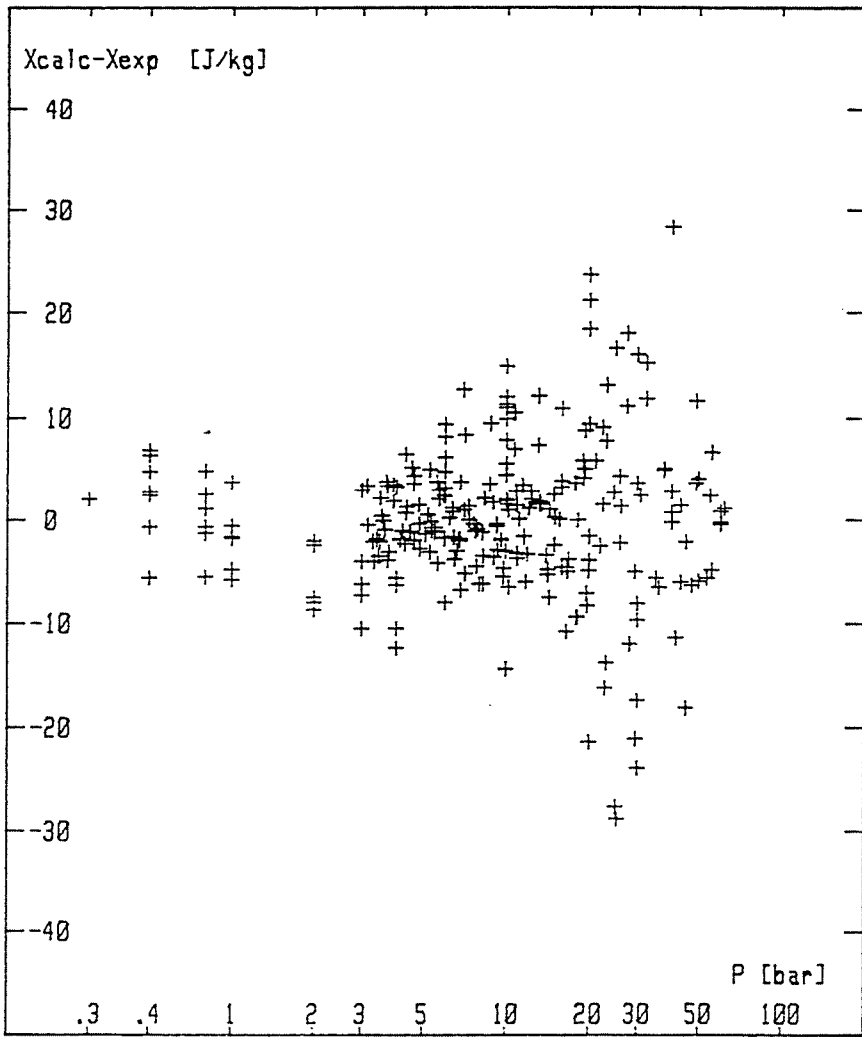


Fig. 4. Deviation from the experimental data at different pressures

The deviations for the different kinds of measurements are as follows:

	Average of the deviations [J/kg]	Average of the absolute values of deviations [J/kg]
c_p measurements	-1.2	6.5
J. T. C. measurements	+6.1	11.0
P - v - T measurements	-0.1	4.3

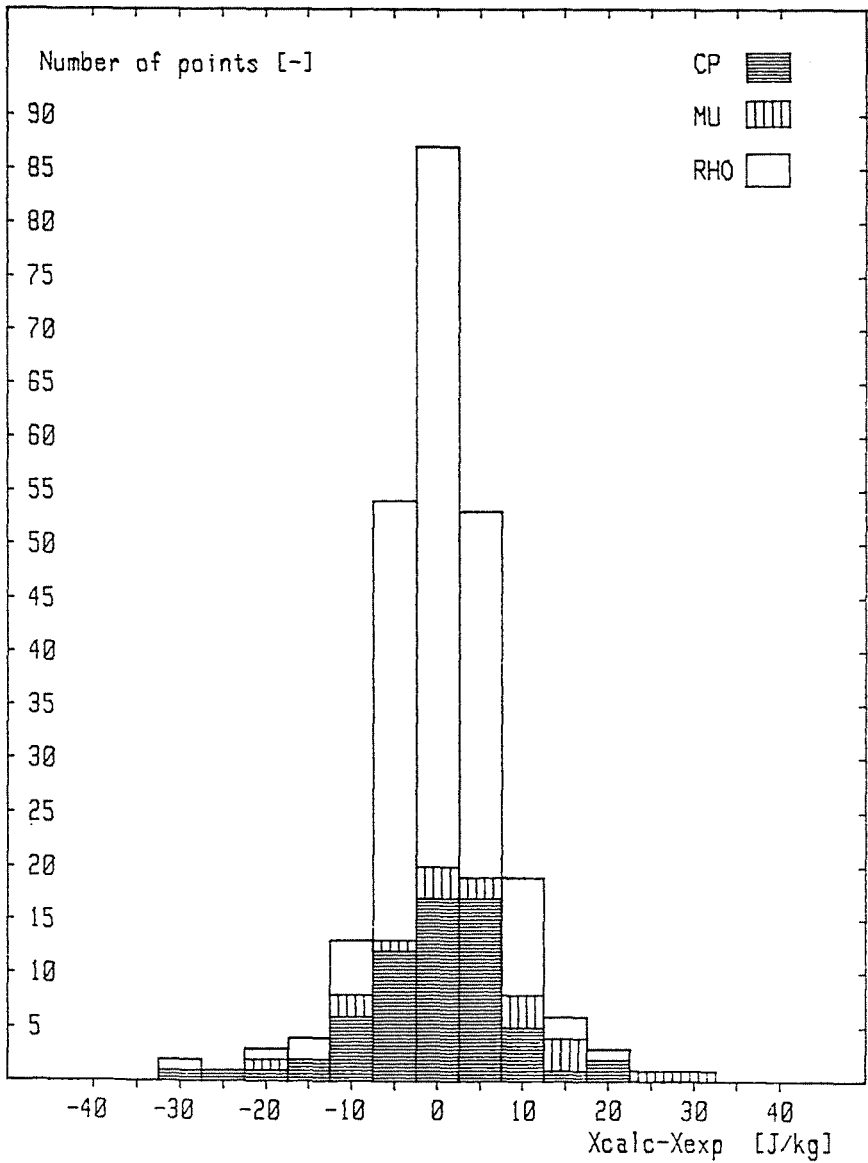


Fig. 5. Distribution of the deviations

It is to be noted that the deviations given above are not the obtainable best values since the calculation was stopped before achieving the minimum of the expression (6).

The slope of the ideal gas isobaric heat capacity function changes relatively rapidly between 90 and 150 °C, where low pressure c_p measurements exist only at 90, 120 and 150 °C.

Several specific heat and J. T. C. data exist in [1] only for higher pressures from 90 to 150 °C. The calculation of the enthalpies for these states using *Eq. (1)* and the minimization of the deviations from the experimental data by *Eq. (2)* means that these data have an influence on the calculated ideal gas isobaric specific function as 'far effect'. This effect may reduce the accuracy of the ideal gas heat capacity function. It seems to be necessary to have some more c_p measurements in this temperature range (perhaps at cca. 105 and 135 °C) at low pressure to improve the correctness of the calculations.

To show the 'far effect', the calculations were carried out using two ideal gas isobaric heat capacity functions differing in the number in their parameters. The number of the parameters allowed the appearance of this effect in one case, but not in the other one. Both runs gave an E. O. S. and an ideal gas isobaric heat capacity function which reproduce the measured data with the deviations given above. The difference of these c_p functions is shown in *Fig. 6*. This shows that the uncertainty of the ideal gas heat capacity may reach 4 J/Kg, K between 120 and 150 °C.

The tabulation of the measured data contains often round pressures and temperatures. Since the measurements happen generally not with these round values, it is necessary to correct the data to the round P, T values. The correction may be done using *Eqs. (3), (4) and (5)* with the calculated constants $A(i)$ to $E(j)$. This has the advantage that the correction happens with values which refer really to the tested medium.

Example 1: The measured c_p value at $P = 20.009$ bar and $t = 101.013$ °C is 1181.0 J/kg, K [1]. The calculation gives for the same conditions 1179.79 J/kg, K and for $P = 20$ bar and $t = 101$ °C 1179.54 J/kg, K. The measured data — corrected to 20 bar and 101 °C — is $1181.0 + (1179.54 - 1179.79) = 1180.75$ J/kg, K.

Example 2: The measured J. T. C. at $P = 6.225$ bar and $t = 120.050$ °C is 0.78716 K/bar [1]. The calculation gives for the same conditions 0.7834 K/bar and for $P = 6$ bar and $t = 120$ °C 0.7816 K/bar. The measured data — corrected to 6 bar and 120 °C — is also $0.78716 + (0.7816 - 0.7834) = 0.78536$ K/bar.

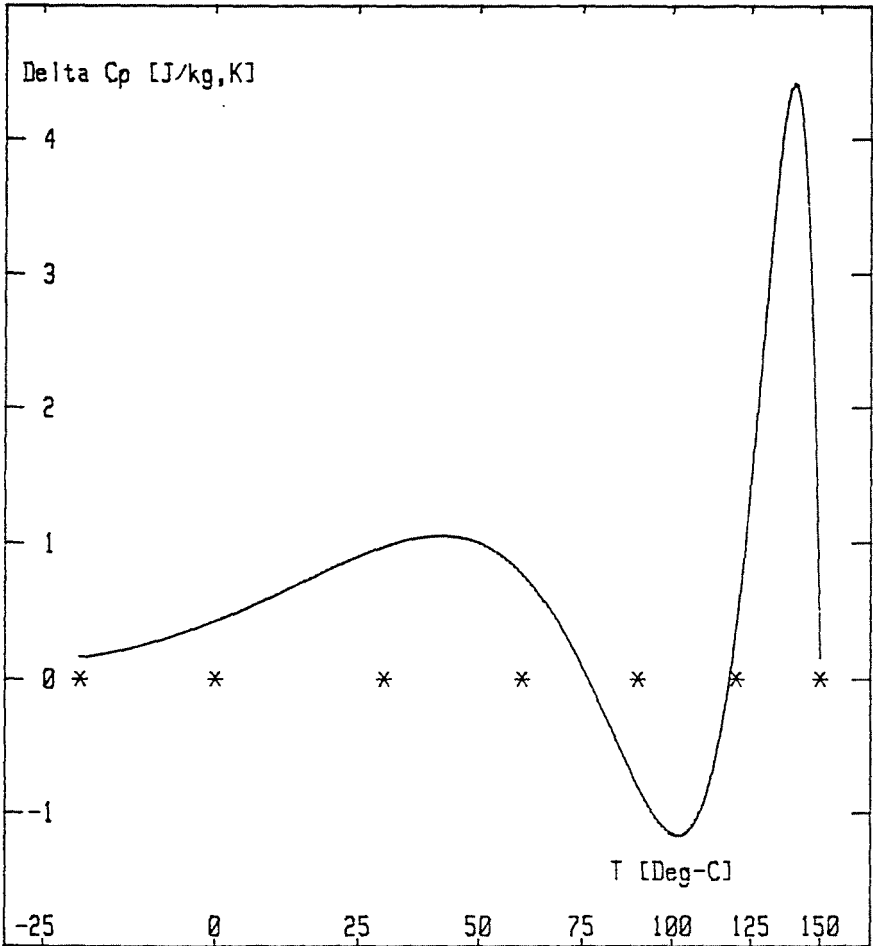


Fig. 6. Difference of the C_p^0 functions at different temperatures

The Basic Function

We tested as basic function the E. O. S. of the ideal gas and some different van der Waals-type equations. The later differ in the number of constants and in that, whether they fulfil the critical conditions or not. All 219 P - v - T data from [2] were used for the testing. The features of the equations

and the average deviations from the measured $P \cdot v$ products are as follows:

Nr.	Type of the E. O. S.	Number of constants	Critical conditions fulfilled	Average deviation from measured data [J/kg]
1	ideal gas	0	NO	4750
2	van der Waals	3	YES	1475
3	van der Waals	5	YES	371
4	van der Waals	4	NO	97
5	van der Waals	7	NO	33

Further calculations show that the 1-st equation of Dieterici (2-nd row) needs 9 correcting terms to approximate the 165 $P-v-T$ data of the gas phase with an average error of 5.5 J/kg; the van der Waals-type equation with 7 constants (5-th row) needs only 4 terms to reach the same accuracy.

Conclusions

The results show that the method presented in this paper is a suitable tool to evaluate simultaneously $P-v-T$, isobaric specific heat and J. T. C. measurements, but the calculation is time consuming. It is practical to choose such a function as basis which approximates the $P-v-T$ data strictly. Furthermore, the method gives the possibility to prepare such a data set for the determination of a pressure-explicit E. O. S. , which set contributes to get an E. O. S. that describes not only the $P-v-T$ relation correctly but the derivatives also.

Nomenclature

P	[N/m ²]	pressure
v	[m ³ /kg]	specific volume
T	[K]	temperature
t	[°C]	temperature
h	[J/kg]	specific enthalpy
c_p	[J/kg, K]	isobaric specific heat
X	[J/kg]	$P \cdot v$ or h
R	[J/kg, K]	gas constant
subscripts	exp	experimental
	calc	calculated
	b	basic

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