

THE EQUATION OF STATE OF CARBON DIOXIDE IN THE TEMPERATURE RANGE 273°-4000° K, FOR PRESSURES UP TO 1000 · 10<sup>5</sup> N/m<sup>2</sup>

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Equations of state have been constructed for carbon dioxide in the temperature range 273°-4000° K and at pressures up to 1000 × 10<sup>5</sup> N/m<sup>2</sup>, giving an accurate description of the gaseous and liquid phases; the left and right boundary curves have also been formed (the first from 273° to 800° K, the second from 770° to 4000° K). There is shown to be good agreement between the calculation quantities and the data of other authors.

In the design of contemporary thermal power plant in which carbon dioxide is used as a working substance or a component of gas mixtures, knowledge is required of a number of thermophysical properties of this substance over a wide range of temperature and pressure. The existing tabulated data [1-5], however, cover narrow ranges of the parameters, have been obtained by various methods, and show poor inter-agreement.

It should be added that following publication of [1-5], experimental investigations were carried out of the compressibility to 1073° K [6], of the velocity of sound [7], of the enthalpy [8], and of the specific heat [9].

The authors of the present paper have correlated all the experimental material and have composed an equation of state which accurately reflects the experimental thermal and caloric data for CO<sub>2</sub>. For temperatures in the range 273°-800° K and pressures in the range 1-100 · 10<sup>5</sup> N/m<sup>2</sup>, the equation was constituted in terms of elementary functions in the form

$$\frac{Pv}{RT_k} = \alpha_0(\omega) + \alpha_1(\omega)\tau + \beta(\omega)\psi + \gamma(\omega)\psi^2 + \delta(\omega)\psi^3 + \lambda(\omega)\psi^4 \tag{1}$$

The elementary functions  $\alpha_0, \alpha_1, \beta, \dots$  have the form

$$A(\omega) = \sum_1^8 a_j \omega^j, \quad \psi = \sum_1^7 b_i \frac{1}{\tau^i}$$

The values of the coefficients of this equation of state are given in the table.

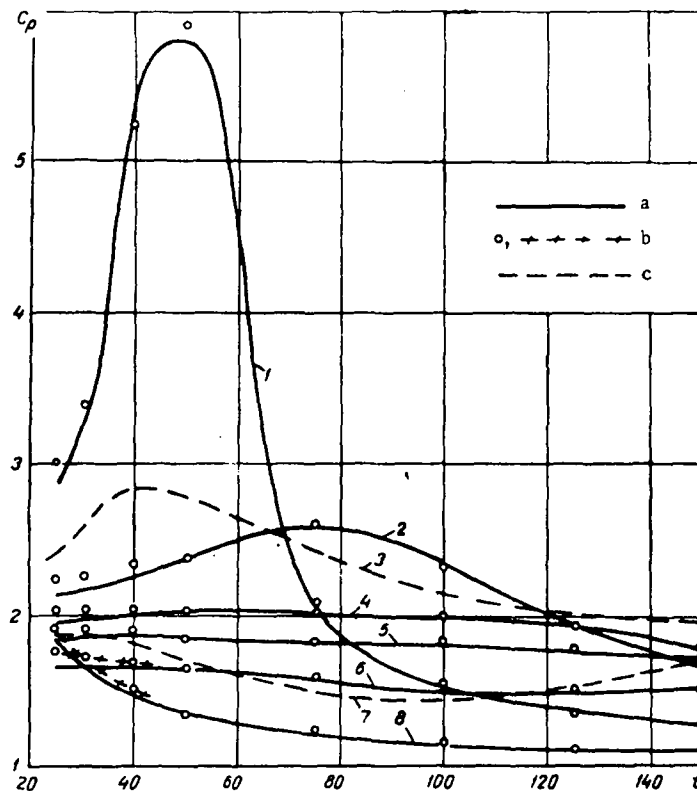


Fig. 1. Comparison of the calculated values of specific heat  $c_p$  (kJ/kg · °K) with the data of [1] and [11]: a) calculated values; b) values of [11]; c) values of [1]; 1) at pressure 101.3 · 10<sup>5</sup> N/m<sup>2</sup>; 2, 3) 202.6 · 10<sup>5</sup>; 4) 303.9 · 10<sup>5</sup>; 5) 405.2 · 10<sup>5</sup>; 6, 7) 1013.0 · 10<sup>5</sup>; 8) 50.65 · 10<sup>5</sup>.

We note that the equation of state (1) accurately describes both the gaseous and the liquid phases of CO<sub>2</sub>, including both boundary curves.

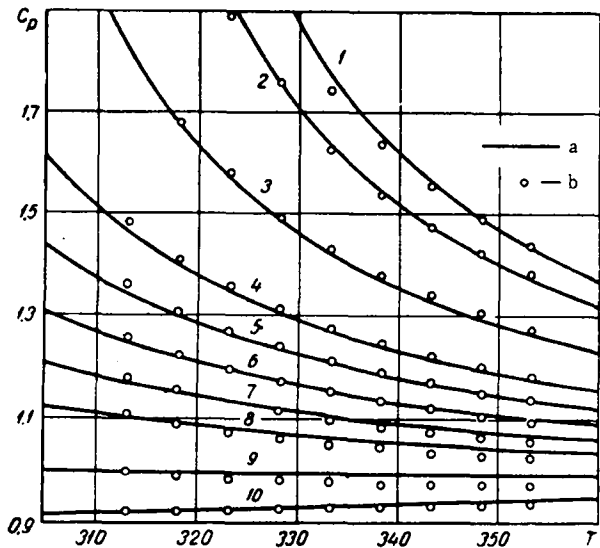


Fig. 2. Comparison of the calculated values of specific heat  $c_p$  (kJ/kg · °K) with the experimental data of [9]: a) calculated values; b) according to [9]; 1) at pressure  $75 \cdot 10^5$  N/m<sup>2</sup>; 2)  $70 \cdot 10^5$ ; 3)  $60 \cdot 10^5$ ; 4)  $50 \cdot 10^5$ ; 5)  $45 \cdot 10^5$ ; 6)  $40 \cdot 10^5$ ; 7)  $35 \cdot 10^5$ ; 8)  $30 \cdot 10^5$ ; 9)  $20 \cdot 10^5$ ; 10)  $10 \cdot 10^5$ .

Analysis shows that, starting from  $T = 770^\circ$  K, for  $P = 1-600 \cdot 10^5$  N/m<sup>2</sup>, it is sufficient to restrict ourselves, in composing the equation of state, to only the two virial coefficients  $B(t)$  and  $C(T)$ .

The virial coefficients were found from the experimental data on compressibility, and were extrapolated into the high temperature region by the method described in [10].

For the region  $T = 770^\circ-4000^\circ$  K and  $P = 1-600 \times 10^5$  N/m<sup>2</sup> of the parameters, the equation of state

was set up in the virial form, reduced to the form

$$\frac{Pv}{RT_*} = \tau + A_1(\tau)\omega + A_2(\tau)\omega^2, \quad (2)$$

where  $A_1 = Bd_c\tau$ ;  $A_2 = Cd_c^2\tau$ .

The coefficients  $A_1$  and  $A_2$  were represented analytically as

$$A_1 = 3.18607 + 0.315748 \cdot \tau - 38.2447 \cdot \frac{1}{\tau} + 176.489 \cdot \frac{1}{\tau^2} - 352.087 \cdot \frac{1}{\tau^3} - 345.939 \cdot \frac{1}{\tau^4} + 3123.11 \cdot \frac{1}{\tau^5} - 5632.78 \cdot \frac{1}{\tau^6} + 3455.76 \cdot \frac{1}{\tau^7};$$

$$A_2 = 1.65195 + 0.0700493 \cdot \tau - 10.5592 \cdot \frac{1}{\tau} + 36.1373 \cdot \frac{1}{\tau^2} - 42.6338 \cdot \frac{1}{\tau^3} - 112.070 \cdot \frac{1}{\tau^4} + 481.306 \cdot \frac{1}{\tau^5} - 673.419 \cdot \frac{1}{\tau^6} + 349.463 \cdot \frac{1}{\tau^7}.$$

The upper limit of temperature,  $4000^\circ$  K, was chosen from considerations of the need to know the properties of CO<sub>2</sub> as a molecular component (without allowing for its dissociation) of the products of combustion of organic fuels, which are investigated ordinarily up to  $T \approx 3000^\circ-4000^\circ$  K.

A verification of (1) and (2) against numerous experimental thermal data has shown that these equations are accurate. The accuracy of description of the most reliable data on compressibility [6, 11-15] is 0.1-0.3% on the average over the whole range of temperature and pressure investigated, including the liquid and the boundary curve, and it is only in the region above critical (at the sections where the isotherms bend) that  $\delta Pv$  reaches 1%.

It should be noted that the method described in [10] allows us to obtain data on compressibility at high temperatures with an accuracy of the order of 0.3-0.5%.

### Elementary Functions of the Equation of State for CO<sub>2</sub>

A(ω)	a <sub>j</sub>			
	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>
z <sub>0</sub>	-0.85458	-22.17446	87.83910	-146.35219
z <sub>1</sub> -1	0.47958	5.50789	-20.57483	33.37070
z <sub>2</sub>	-1.0	57.43943	-244.48793	433.35161
z <sub>3</sub>	0.0	-92.26009	428.77893	-808.57578
z <sub>4</sub>	0.0	81.74075	-399.97908	786.20898
λ	0.0	-29.18432	146.42342	-294.20948

A(ω)	a <sub>j</sub>			
	a <sub>5</sub>	a <sub>6</sub>	a <sub>7</sub>	a <sub>8</sub>
z <sub>0</sub>	119.56036	-49.63126	9.82473	-0.70584
z <sub>1</sub> -1	-26.22077	10.30618	-1.85624	0.10858
z <sub>2</sub>	-380.36551	173.60427	-39.45155	3.52616
z <sub>3</sub>	755.08893	-370.20358	91.72708	-9.09828
z <sub>4</sub>	-764.12226	390.69253	-101.22791	10.51747
λ	292.68927	-153.36325	40.73115	-4.33421

$$\psi = 7.83210 \cdot \frac{1}{\tau} - 68.39111 \cdot \frac{1}{\tau^2} + 244.51409 \cdot \frac{1}{\tau^3} - 431.55322 \cdot \frac{1}{\tau^4} + 414.36614 \cdot \frac{1}{\tau^5} - 203.12293 \cdot \frac{1}{\tau^6} + 40.23993 \cdot \frac{1}{\tau^7}$$

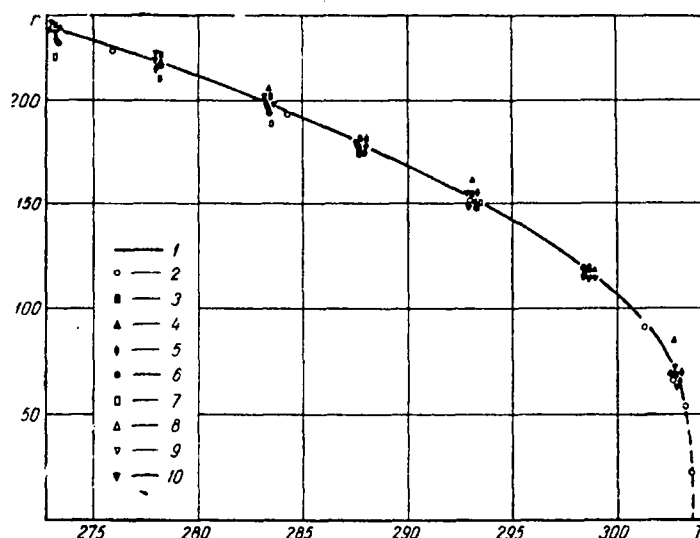


Fig. 3. Dependence of the latent heat of evaporation  $r$  (kJ/kg) of carbon dioxide on temperature: 1) calculated values; 2) values of Michels [11]; 3) -- Vargaftik [2]; 4) Newitt et al. [1]; 5, 6, 7, 8, 9, 10-- respectively, Molier, Langen, Jenkins and Pai, Kees, Eikelberg, and Planck and Kupriyapov [19].

From the well-known differential relations of thermodynamics, on the basis of the equations of state that have been obtained, the calorific data were calculated for  $\text{CO}_2$ .

It is of interest to analyze and compare the caloric quantities resulting from the calculation with the available experimental and handbook data.

Comparison of the calculated values of enthalpy and entropy with the data of [1-5, 8, 16, 17] in the temperature range  $273^\circ\text{--}1500^\circ\text{K}$ , and at pressures up to  $1000 \cdot 10^5 \text{ N/m}^2$  has shown that the discrepancy in enthalpy is 0.5-4.0 kJ/kg, and of entropy--up to 0.3%.

Comparison of the experimental and tabulated values of the specific heat  $c_p$  [1-5, 9, 16] with the calculated values has shown that at an overwhelming majority of points, the deviations from the latest experimental measurements of  $c_p$  [9], and from the tabulated data of [3, 5, 16] do not exceed 1% (this is shown partially in Fig. 1.2).

The experimental measurements of specific heat in the saturated state,  $c'_s$ , [18] agree with the calculated values to 0.5%.

The high accuracy of the calculated values of the thermodynamic properties in the saturated state is confirmed by the fact that the heat of evaporation calculated according to the equation of state (1),  $r = i'' - i'$ , is in good agreement with the data of [1, 2, 11, 19] (see Fig. 3).

As a result of the analysis that was conducted, it was established that the tabulated values of  $c_p$  [1] cannot be regarded as reliable.

We note that the calculated and experimental values of the velocity of sound [7] are in good agreement in the whole single-phase region, including the critical region. The majority of the experimental values differ from those calculated by amounts up to 1%.

The good agreement of the calculated values, evaluated from the equations of state (1) and (2) with the various experimental and tabulated data, gives cause to believe that these equations are reliable. We used them to calculate detailed tables of specific volumes, enthalpy, entropy, specific heat  $c_p$ , velocity of sound, and adiabatic index. These calculations were performed on an electronic computer.

The thermodynamic quantities in the ideal gas state were obtained from [20].

The critical parameters for  $\text{CO}_2$  are:  $T_c = 304.19^\circ\text{K}$ ;  $P_c = 73.816 \cdot 10^5 \text{ N/m}^2$ ;  $d_c = 0.4682 \text{ g/cm}^3$ .

NOTATION

$$\omega = d/d_c; \tau = T/T_c; \pi = P/P_c.$$

REFERENCES

1. F. Din, Thermodynamic Functions of Gases, 1, London, 1956.
2. Thermophysical Properties of Substances, Handbook, ed. N. B. Vargaftik [in Russian], Gosenergoizdat, 1956.
3. A. Michels, Appl. Sc. Res., A1, 1947.
4. Tables of Thermal Properties of Gases, NBS, Circ, 564, 1955.
5. K. E. MacCormack and W. G. Schneider, J. chem. Phys., 18, 126, 1950.
6. M. P. Vukalovich, V. V. Altunin, and N. I. Timoshenko, Teploenergetika, no. 5, 1962, no. 1, 2, 1963.
7. I. I. Novikov and Yu. S. Trelin, Teploenergetika no. 2, 1962.
8. M. P. Vukalovich and Ya. F. Masalov, Teploenergetika, no. 11, 1964.

9. M. P. Vukalovich, V. V. Altunin, and A. N. Gureev, *Teploenergetika*, no. 9, 1964.
10. P. M. Kessel'man, *Teplofizika vysokix temperatur*, no. 9, 1964.
11. A. Michels, B. Blaisse, and G. Michels, *Proc. Roy Soc.*, **A160**, 358, 1937.
12. A. Michels and G. Michels, *Proc. Roy Soc.*, **A153**, 201, 1935.
13. A. Michels and G. Michels, *Proc. Roy Soc.*, **A160**, 348, 1937.
14. A. Michels and H. Wouters, *Proc. Roy Soc.*, **A153**, 214, 1935.
15. C. F. Jenkin, *Proc. Roy Soc.*, **A98**, 170, 1920.
16. O. Price, *Industrial and Engineering Chemistry*, **47**, no. 8, 1955.
17. M. P. Vukalovich, V. V. Altunin, and N. I. Timoshenko, *Atomnaya energiya*, **15**, no. 3, 1963.
18. Eucken and Hauck, **134**, 161, 1928.
19. E. L. Quinn and C. L. Jones, *Carbon dioxide*, New York, 1936.
20. *Thermophysical Properties of Individual Substances, Handbook*, ed. V. P. Glushko, L. V. Gurvich, et al. [in Russian], Moscow, 1962.

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