THERMODYNAMIC PROPERTIES OF GASEOUS PROPANE AND PROPENE

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Based upon the most probable and additional recommended values with respect to the compressibility factor of propane and propene proposed by the High Pressure Data Center of Japan (HPDCJ), new thermodynamic formulations are devised for these substances in their gaseous phases covering the range of temperature from 273.15 K to 523.15 K and pressures up to 30 MPa for propane and also that of temperature from 248.15 K to 498.15 K and pressures up to 60 MPa for propene, respectively. Using the formulated equations of state, the basic correlating functions for these hydrocarbons are derived and then the essential thermodynamic properties such as molar volume, enthalpy, entropy and isobaric specific heat capacity can be calculated.

Introduction

According to the critical evaluation of the available P–V–T property data, the most probable and additional recommended compressibility factor values for propane and propene were proposed by Date and Iwasaki[1] after the discussions at the HPDCJ organized in the Society of Materials Science, Japan, under the sponsorship of the Agency of Science and Technology. The covered range of the state parameters of this previous work was 248.15–548.15 K and pressures up to 30 MPa for propane, whereas 248.15–498.15 K and pressures up to 60 MPa for propene. As a next procedure of the program of the HPDCJ, new equations of state for both propane and propene are formulated based upon these most probable compressibility factor values for the purpose of calculating the P–V–T property values as well as other thermodynamic property values at respective thermodynamic states. In the present paper, these new equations of state which can cover the range of temperatures 273.15–523.15 K and of pressures up to 30 MPa for propane, and also that of temperature 248.15–498.15 K and of pressures up to 60 MPa for propene are described. Moreover, the numerical tables of the important derived thermodynamic property values are also presented for these two different hydrocarbons.

New Equations of State

The so-called skeleton table values of the compressibility factor for propane and propene are composed of the most probable and additional recommended values proposed by the HPDCJ and their covering ranges are shown in Figs. 1 and 2, respectively. It is needless to say that these skeleton table

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1) K. Date and H. Iwasaki, *This Journal*, **44**, 1 (1974)
2) A. P. Kudchadker, G. H. Alani and B. J. Zwolinski, *Chem. Rev.*, **68**, 659 (1968)

values are accompanied by the estimated uncertainties as in the previous skeleton tables for methane[3], ethane and ethene[4]. In the present study, both of the most probable and additional recommended values were used as the basic data sets in devising the new equations of state, in addition to using the estimated uncertainties mentioned above as the criteria for judging the devised equations.

As shown in Fig. 1, the skeleton table of compressibility factor for propane includes those even in the liquid phase and therefore those data below 373.15 K were excluded to be covered by the present formulation beforehand. It is also noteworthy that the present equations of state have to be formulated as a function of density and temperature, since they must cover such wider ranges of the state para-

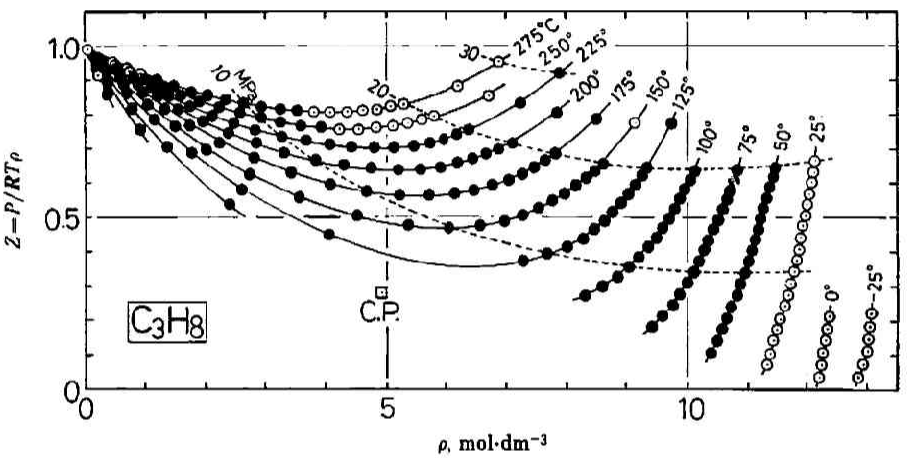

Fig. 1 The most probable and additional recommended compressibility factor values for propane
● most probable values
⊙ additional recommended values
⊡ critical point (369.82 K, 4.250 MPa, 4.92 mol·dm^{-3})[2]

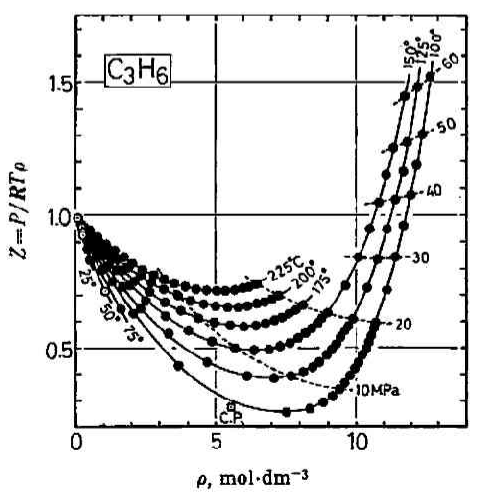

Fig. 2 The most probable and additional recommended compressibility factor values for propene
● most probable values
⊙ additional recommended values
⊡ critical point (365.0 K, 4.62 MPa, 5.54 mol·dm^{-3})[2]

3) J. Osugi, Y. Takezaki and T. Makita, *This Journal*, **41**, 60 (1971)
4) K. Date, K. Watanabe and M. Uematsu, *ibid.*, **43**, 92 (1973)

meters as shown in Figs. 1 and 2. Although it is well known that the Benedict-Webb-Rubin (BWR) equation of state may correlate the P-V-T properties of simple hydrocarbons, it was experienced in

Table 1 Numerical constants in Eqs. (1) and (2) for propane and propene

	Propane	Propene		Propane	Propene
a_1	$-4.090\ 9899\times10^{2}$	$1.770\ 6253\times10^{3}$	a_{17}	0	$4.937\ 6880\times10^{15}$
a_2	$6.221\ 3928\times10^{5}$	$-1.407\ 2709\times10^{6}$	a_{18}	0	$-1.821\ 7334\times10^{19}$
a_3	$-4.269\ 9835\times10^{11}$	$2.815\ 5700\times10^{10}$	a_{19}	$-2.782\ 3613\times10^{19}$	$2.140\ 9060\times10^{21}$
a_4	$6.987\ 0832\times10^{16}$	$-1.982\ 3817\times10^{15}$	a_{20}	$-1.848\ 2512\times10^{14}$	$2.560\ 2341\times10^{15}$
a_5	$-6.741\ 6069\times10^{21}$	$-8.976\ 3010\times10^{19}$	a_{21}	$8.302\ 6578\times10^{15}$	$-2.976\ 8160\times10^{18}$
a_6	$2.827\ 2012\times10^{26}$	$5.317\ 8698\times10^{24}$	a_{22}	0	$1.138\ 5003\times10^{21}$
a_7	$-2.187\ 7931\times10^{35}$	0	a_{23}	0	$-1.417\ 9285\times10^{23}$
a_8	$-1.294\ 8332\times10^{5}$	$-7.567\ 4088\times10^{5}$	a_{24}	$3.341\ 9911\times10^{5}$	0
a_9	$3.186\ 4286\times10^{8}$	$7.109\ 3220\times10^{8}$	a_{25}	$-4.064\ 7594\times10^{8}$	0
a_{10}	0	$-1.505\ 5735\times10^{11}$	a_{26}	$6.923\ 3929\times10^{13}$	$4.048\ 8404\times10^{12}$
a_{11}	$-4.590\ 3560\times10^{13}$	$-7.422\ 0764\times10^{11}$	a_{27}	$-1.458\ 5349\times10^{18}$	0
a_{12}	$1.728\ 3452\times10^{7}$	$2.325\ 5824\times10^{8}$	γ	$1.944\ 4748\times10^{4}$	$2.479\ 0640\times10^{4}$
a_{13}	$2.448\ 3052\times10^{10}$	$-1.617\ 1961\times10^{11}$	c_1	$3.663\ 65\times10^{0}$	$3.209\ 14\times10^{1}$
a_{14}	$1.020\ 5948\times10^{15}$	$1.150\ 2383\times10^{16}$	c_2	$2.547\ 41\times10^{-1}$	$4.724\ 83\times10^{-2}$
a_{15}	$3.160\ 9572\times10^{22}$	$-4.218\ 4990\times10^{22}$	c_3	$-5.758\ 13\times10^{-5}$	$2.714\ 90\times10^{-4}$
a_{16}	$1.455\ 4779\times10^{12}$	$-4.297\ 6459\times10^{13}$	c_4	$-3.047\ 05\times10^{-8}$	$-2.328\ 43\times10^{-7}$

Table 2 Average deviations of the compressibility factor values for propane and propene from Eq. (1)

	Available data sources	Number of data points compared	Average deviation* (%)
Propane	Skeleton table values[1]	178	0.092
	Sage *et al.* (1934)[10]	56	0.944
	Beattie *et al.* (1937)[11]	87	0.163
	Deschner *et al.* (1940)[12]	147	0.700
	Lu (1940)[13]	—	—**
	Reamer *et al.* (1949)[14]	164	0.133
	Cherney *et al.* (1946)[15]	15	0.359
Propene	Skeleton table values[1]	167	0.057
	Farrington *et al.* (1949)[16]	194	0.121
	Marchman *et al.* (1949)[17]	202	0.118
	Michels *et al.* (1953)[18]	190	0.054

* Calculated by the expression given below:

$$\sigma\,(\%)=\frac{\Sigma\,|\,(Z_{exp}-Z_{cal})/Z_{cal}\,|\times100}{n},$$

where Z_{exp}=reported compressibility factor values,
Z_{cal}=calculated values by Eq. (1),
n=number of data points compared.

** Reported data by Lu are in liquid phases where the present formulation is not effective.

Table 3-1 Calculated values of compressibility factor Z of gaseous propane and their comparison with the skeleton table values

Pressure	Temperature K (°C)				
MPa	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)
0.1	0.97913 0.97948 -0.035/0.040	0.98440 0.98392 0.049/0.040	0.98787 0.98737 0.051/0.040	0.99028 0.99000 0.028/0.040	0.99204 0.99198 0.006/0.040
0.5		0.9119 0.91433 -0.265/0.35	0.9348 0.93403 0.082/0.25	0.9487 0.94851 0.020/0.20	0.9591 0.95911 -0.001/0.15
1			0.8599 0.85913 0.089/0.25	0.8927 0.89262 0.009/0.30	0.9140 0.91599 -0.217/0.35
2				0.7565 0.75956 -0.403/0.50	0.8194 0.82064 -0.151/0.50
3					0.7057 0.70516 0.077/0.30
4					0.5380 0.53599 0.375/0.30

[ ]: the most probable values

1st line : skeleton table value, Z_{ST}

2nd line : calculated value, Z_{cal}

3rd line : deviation(%)/uncertainty(%)

deviation(%)=$[(Z_{ST}-Z_{cal})/Z_{cal}]\times 100$

our previous work[5] that several additional terms were required to the original BWR equation in order to cover wider range of the present interest.

Hence, after several possible additional terms had been tested taking into consideration the possibility for obtaining a common functional form for both substances, the following functional form which was developed from the original BWR equation was adopted for the present purpose:

$$\begin{aligned} P=&RT\rho+(a_1T+a_2+a_3/T^2+a_4/T^4+a_5/T^6+a_6/T^8+a_7/T^{12})\rho^2 \\ &+(a_8T+a_9+a_{10}/T+a_{11}/T^2)\rho^3+(a_{12}T+a_{13}+a_{14}/T^2+a_{15}/T^5)\rho^4 \\ &+(a_{16}+a_{17}/T+a_{18}/T^2+a_{19}/T^3)\rho^5+(a_{20}+a_{21}/T+a_{22}/T^2+a_{23}/T^3)\rho^6 \\ &+(a_{24}T+a_{25}+a_{26}/T^2+a_{27}/T^4)\rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2), \end{aligned} \tag{1}$$

where P=pressure in MPa, T=temperature in K, $T=t+273.15$, t=temperature in °C on IPTS-68, ρ=molar density in mol·cm^{-3}, R=molar gas constant in J·K^{-1}mol^{-1}, and $a_1, a_2, \cdots, a_{27}, \gamma$=numerical constants.

The following values were adopted as the atomic weights recommended by IUPAC[6] as well as the molar gas constant recommended by CODATA[7]:

$$C=\ 12.011\ \ \pm 0.001\,,$$

5) M. Uematsu, S. Saegusa, K. Watanabe and I. Tanishita, *This Journal*, **45**, 53 (1975)

6) *Pure and Appl. Chem.*, **37**, 589 (1974)

7) *CODATA Bull.*, No. 11 (1973)

Table 3-2 (continued)

Pressure	Temperature K (°C)					
MPa	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)	523.15 (250)
0.1	0.99339	0.99448	0.99539	0.99620	0.99691	0.99757
	0.99348	0.99464	0.99555	0.99629	0.99688	0.99737
	-0.009/0.040	-0.016/0.040	-0.016/0.040	-0.009/0.040	0.003/0.040	0.020/0.040
0.5	0.9672	0.9727	0.9773	0.9813	0.9845	0.9867
	0.96699	0.97300	0.97770	0.98144	0.98445	0.98692
	0.022/0.10	-0.031/0.10	-0.041/0.10	-0.014/0.10	0.005/0.10	-0.022/0.15
1	0.9328	0.9451	0.9550	0.9629	0.9693	0.9713
	0.93286	0.94549	0.95521	0.96288	0.96903	0.97402
	-0.007/0.10	-0.041/0.10	-0.022/0.10	0.002/0.10	0.028/0.10	-0.279/0.15
2	0.8623	0.8893	0.9096	0.9257	0.9389	0.9484
	0.86049	0.88867	0.90965	0.92582	0.93858	0.94881
	0.211/0.10	0.071/0.10	-0.006/0.10	-0.013/0.15	0.034/0.15	-0.043/0.15
3	0.7826	0.8299	0.8629	0.8891	0.9097	0.9240
	0.78069	0.82902	0.86327	0.88891	0.90876	0.92447
	0.244/0.10	0.106/0.10	-0.043/0.10	0.022/0.15	0.104/0.15	-0.051/0.15
4	0.6894	0.7663	0.8161	0.8527	0.8811	0.9015
	0.68958	0.76589	0.81607	0.85227	0.87970	0.90111
	-0.026/0.15	0.054/0.10	0.004/0.10	0.051/0.15	0.159/0.15	0.044/0.15
5	0.5799	0.6973	0.7680	0.8160	0.8521	0.8784
	0.57959	0.69864	0.76817	0.81611	0.85157	0.87884
	0.054/0.30	-0.192/0.10	-0.022/0.10	-0.014/0.15	0.062/0.15	-0.050/0.15
6	0.4474	0.6258	0.7198	0.7804	0.8244	0.8567
	0.44589	0.62763	0.72010	0.78079	0.82460	0.85780
	0.338/0.30	-0.292/0.20	-0.042/0.15	-0.050/0.15	-0.024/0.15	-0.129/0.20
7		0.5583	0.6726	0.7467	0.7985	0.8375
		0.55763	0.67320	0.74690	0.79909	0.83817
		0.120/0.50	-0.089/0.20	-0.027/0.15	-0.074/0.15	-0.080/0.20
8		0.5028	0.6284	0.7160	0.7753	0.8206
		0.50290	0.63026	0.71540	0.77547	0.82015
		-0.021/0.50	-0.295/0.40	0.084/0.15	-0.021/0.15	0.055/0.20
9	0.3726	0.4753	0.5945	0.6885	0.7542	0.8048
	0.37102	0.47533	0.59557	0.68762	0.75425	0.80398
	0.426/0.40	-0.006/0.50	-0.180/0.25	0.128/0.10	-0.007/0.20	0.103/0.25
10	0.3920	0.4691	0.5740	0.6661	0.7364	0.7903
	0.39113	0.46953	0.57278	0.66513	0.73607	0.78992
	0.222/0.60	-0.092/0.45	0.213/0.15	0.145/0.10	0.044/0.15	0.048/0.25
11	0.4138	0.4747	0.5646	0.6515	0.7211	0.7783
	0.41422	0.47613	0.56224	0.64920	0.72156	0.77826
	-0.100/0.45	-0.300/0.25	0.421/0.15	0.355/0.10	-0.063/0.15	0.005/0.15
12	0.4372	0.4885	0.5632	0.6424	0.7107	0.7689
	0.43874	0.48944	0.56153	0.64022	0.71117	0.76926
	-0.351/0.30	-0.191/0.20	0.297/0.20	0.340/0.25	-0.066/0.15	-0.046/0.15
13	0.4635	0.5064	0.5670	0.6378	0.7046	0.7625
	0.46403	0.50654	0.56775	0.63769	0.70511	0.76308
	-0.113/0.30	-0.028/0.30	-0.131/0.20	0.018/0.35	-0.072/0.25	-0.077/0.20
14	0.4893	0.5272	0.5785	0.6394	0.7023	0.7596
	0.48972	0.52592	0.57861	0.64050	0.70323	0.75981
	-0.086/0.30	0.244/0.20	-0.020/0.15	-0.171/0.20	-0.133/0.15	-0.027/0.20

Table 3-3 (continued)

Pressure	Temperature K (°C)					
MPa	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)	523.15 (250)
15	0.5157	0.5482	0.5924	0.6462	0.7036	0.7588
	0.51563	0.54671	0.59260	0.64748	0.70514	0.75936
	0.013/0.30	0.273/0.20	-0.034/0.10	-0.198/0.25	-0.218/0.15	-0.074/0.20
16	0.5417	0.5692	0.6085	0.6573	0.7089	0.7607
	0.54165	0.56841	0.60872	0.65760	0.71027	0.76157
	0.009/0.20	0.138/0.25	-0.037/0.10	-0.046/0.30	-0.193/0.20	-0.114/0.20
17	0.5680	0.5909	0.6265	0.6702	0.7174	0.7654
	0.56770	0.59072	0.62632	0.67006	0.71868	0.76617
	0.053/0.20	0.030/0.30	0.029/0.10	0.021/0.10	-0.094/0.20	-0.100/0.20
18	0.5942	0.6131	0.6451	0.6844	0.7286	0.7726
	0.59374	0.61344	0.64497	0.68426	0.72803	0.77286
	0.078/0.20	-0.055/0.35	0.021/0.10	0.020/0.25	0.078/0.15	-0.034/0.20
19	0.6205	0.6355	0.6641	0.6992	0.7406	0.7820
	0.61974	0.63642	0.66437	0.69977	0.73970	0.78134
	0.123/0.30	-0.145/0.35	-0.040/0.10	-0.081/0.20	0.121/0.20	0.084/0.20
20	0.6466	0.6586	0.6843	0.7158	0.7538	0.7931
	0.64568	0.65959	0.68431	0.71626	0.75273	0.79133
	0.143/0.45	-0.150/0.35	-0.002/0.10	-0.064/0.20	0.142/0.20	0.224/0.20
25	0.7730	0.7772	0.7878	0.8072	0.8309	0.8558
	0.77417	0.77638	0.78833	0.80704	0.83022	0.85627
	-0.152/0.50	0.106/0.40	-0.067/0.25	0.020/0.20	0.082/0.20	-0.055/0.20
30					0.9179	
					0.91728	
					0.068/0.10	

[ ]: the most probable values
1st line : skeleton table value, Z_{ST}
2nd line : calculated value, Z_{cal}
3rd line : deviation(%)/uncertainty(%); deviation(%)=$[(Z_{ST}-Z_{cal})/Z_{cal}]\times100$

$$H = 1.0079 \pm 0.0001 ,$$

$$R = 8.31441 \pm 0.00026 \ J \cdot K^{-1} mol^{-1} .$$

In the procedure of determining the numerical constants in Eq. (1), the skeleton table values were introduced as a set of input data into a least-square processing and the characteristic behavior of the computed isobaric specific heat capacity values were also carefully examined. Especially, the reported experimental values by Bier *et al.*[8] for propene in the range of temperature 298.15 K–473.15 K and pressures up to 12 MPa were taken into consideration for the present purpose. As a result of these procedures, the numerical constants for both propane and propene in Eq. (1) were fixed on as listed in Table 1.

In case of computing the isobaric specific heat capacity, the following correlations for the isobaric specific heat capacity at the ideal gas state, C_p^0, devised by Makita[9] were used:

$$C_p^0 = c_1 + c_2 T + c_3 T^2 + c_4 T^3 . \qquad (2)$$

The numerical constants which appeared in Eq. (2) are also tabulated for both propane and propene

8) K. Bier, G. Ernst, J. Kunze and G. Maurer, *J. Chem. Thermodynamics*, 6, 1039 (1974)
9) T. Makita, private communication to the present author

Table 4-1 Calculated values of compressibility factor Z of gaseous propene and their comparison with the skeleton table values

Pressure	Temperature K (°C)										
MPa	248.15 (-25)	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
0.1	0.97481	0.98151	0.98602	0.98919	0.99148	0.99317	0.99444	0.99543	0.99623	0.99689	0.99746
	0.97471	0.98129	0.98588	0.98907	0.99136	0.99305	0.99435	0.99536	0.99617	0.99684	0.99739
	0.010/0.020	0.022/0.020	0.014/0.020	0.012/0.020	0.012/0.020	0.012/0.020	0.009/0.020	0.007/0.020	0.006/0.020	0.005/0.020	0.007/0.020
0.5			0.9246	0.9450	0.9591	0.9640	0.9714	0.9767	0.9812	0.9847	0.9870
			0.92512	0.94311	0.95558	0.96459	0.97137	0.97662	0.98078	0.98415	0.98692
			-0.056/0.10	0.200/0.10	0.369/0.10	-0.061/0.10	0.003/0.10	0.009/0.10	0.043/0.10	0.056/0.10	0.008/0.10
1			0.8354	0.8792	0.9073	0.9274	0.9418	0.9530	0.9618	0.9692	0.9740
			0.83579	0.87937	0.90765	0.92735	0.94177	0.95274	0.96133	0.96821	0.97382
			-0.047/0.10	-0.019/0.10	-0.039/0.10	0.006/0.10	0.003/0.10	0.027/0.10	0.049/0.10	0.102/0.10	0.018/0.10
2				0.7154	0.7972	0.8455	0.8792	0.9035	0.9221	0.9370	0.9477
				0.71433	0.79670	0.84585	0.87917	0.90336	0.92172	0.93610	0.94763
				0.150/0.25	0.062/0.10	-0.041/0.10	0.003/0.10	0.015/0.10	0.041/0.10	0.097/0.10	0.008/0.10
3					0.6450	0.7508	0.8108	0.8517	0.8811	0.9039	0.9212
					0.64574	0.75080	0.81092	0.85155	0.88115	0.90374	0.92152
					-0.115/0.10	0.000/0.10	-0.015/0.10	0.018/0.10	-0.006/0.10	0.018/0.10	-0.035/0.10
4						0.6308	0.7355	0.7966	0.8385	0.8718	0.8962
						0.63083	0.73508	0.79698	0.83986	0.87127	0.89566
						-0.005/0.20	0.057/0.10	-0.048/0.10	-0.141/0.20	0.061/0.10	0.061/0.15
5							0.6492	0.7390	0.7966	0.8385	0.8697
							0.64872	0.73947	0.79751	0.83893	0.87023
							0.075/0.10	-0.064/0.10	-0.114/0.20	-0.052/0.10	-0.061/0.10
6							0.5506	0.6786	0.7541	0.8073	0.8453
							0.54896	0.67938	0.75510	0.80707	0.84551
							0.299/0.10	-0.115/0.25	-0.133/0.25	0.028/0.10	-0.025/0.10
7							0.4488	0.6184	0.7123	0.7767	0.8219
							0.44790	0.61875	0.71339	0.77623	0.82183
							0.201/0.10	-0.057/0.35	-0.153/0.35	0.061/0.10	0.008/0.10
8							0.3931	0.5635	0.6737	0.7480	0.7998
							0.39324	0.56323	0.67401	0.74713	0.79960
							-0.035/0.10	0.048/0.20	-0.047/0.30	0.117/0.10	0.025/0.10
9							0.3841	0.5223	0.6402	0.7212	0.7790
							0.38407	0.52155	0.63933	0.72069	0.77927
							0.009/0.15	0.144/0.10	0.135/0.10	0.070/0.10	-0.035/0.10
10							0.3932	0.4990	0.6132	0.6980	0.7609
							0.39310	0.49851	0.61186	0.69793	0.76133
							0.024/0.10	0.099/0.10	0.220/0.10	0.009/0.10	-0.056/0.15
11							0.4091	0.4908	0.5943	0.6791	0.7457
							0.40926	0.49132	0.59313	0.67971	0.74619
							-0.039/0.10	-0.106/0.10	0.198/0.10	-0.090/0.10	-0.066/0.20
12							0.4284	0.4938	0.5833	0.6662	0.7344
							0.42867	0.49468	0.58310	0.66653	0.73418
							-0.063/0.10	-0.178/0.10	0.035/0.10	-0.050/0.10	0.030/0.25

: the most probable values
1st line : skeleton table value, Z_{ST}
2nd line : calculated value, Z_{cal}
3rd line : deviation(%)/uncertainty(%)
deviation(%)=$[(Z_{ST}-Z_{cal})/Z_{cal}]\times 100$

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Table 4-2 (continued)

Pressure	Temperature K (°C)				
MPa	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
13	0.4496	0.5042	0.5798	0.6584	0.7262
	0.44976	0.50450	0.58052	0.65845	0.72546
	-0.036/0.15	-0.059/0.10	-0.124/0.15	-0.008/0.10	0.103/0.20
14	0.4718	0.5182	0.5830	0.6552	0.7204
	0.47179	0.51825	0.58376	0.65511	0.72001
	0.002/0.20	-0.009/0.15	-0.130/0.15	0.014/0.10	0.054/0.15
15	0.4949	0.5341	0.5912	0.6560	0.7175
	0.49435	0.53447	0.59132	0.65591	0.71768
	0.110/0.25	-0.069/0.10	-0.020/0.15	0.014/0.10	-0.026/0.15
16	0.5177	0.5523	0.6024	0.6604	0.7176
	0.51723	0.55229	0.60202	0.66019	0.71823
	0.090/0.20	0.003/0.15	0.063/0.15	0.031/0.10	-0.087/0.15
17	0.5404	0.5717	0.6158	0.6670	0.7205
	0.54029	0.57116	0.61501	0.66731	0.72133
	0.020/0.20	0.094/0.20	0.129/0.30	-0.047/0.10	-0.115/0.15
18	0.5633	0.5911	0.6304	0.6767	0.7266
	0.56344	0.59076	0.62965	0.67670	0.72667
	-0.024/0.20	0.057/0.20	0.119/0.30	0.000/0.10	-0.009/0.15
19	0.5863	0.6110	0.6455	0.6872	0.7344
	0.58662	0.61086	0.64552	0.68790	0.73392
	-0.054/0.20	0.023/0.20	-0.003/0.20	-0.102/0.10	0.065/0.20
20	0.6094	0.6312	0.6620	0.7000	0.7438
	0.60980	0.63130	0.66230	0.70053	0.74281
	-0.065/0.20	-0.016/0.20	-0.045/0.25	-0.076/0.10	0.133/0.20
25	0.7251	0.7359			
	0.72497	0.73587			
	0.018/0.15	0.004/0.15			
30	0.8382	0.8412			
	0.83829	0.84112			
	-0.011/0.15	0.009/0.10			
35	0.9494	0.9453			
	0.94959	0.94547			
	-0.020/0.15	-0.018/0.10			
40	1.0588	1.0479			
	1.05897	1.04850			
	-0.016/0.15	-0.057/0.15			
45	1.1665	1.1501			
	1.16660	1.15012			
	-0.008/0.20	-0.002/0.20			
50	1.2727	1.2505			
	1.27263	1.25037			
	0.006/0.20	0.011/0.20			
60	1.4806	1.4474			
	1.48043	1.44704			
	0.011/0.20	0.025/0.20			

in Table 1.

Comparison of the compressibility factor values computed from Eq. (1) with the skeleton table values and also with the experimental data of both propane[10-15] and propene[16-18] were conducted. It

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Table 5 Numerical constants in Eq. (3) for propane and propene

	Propane	Propene		Propane	Propene
d_1	$-1.184\ 5823\times10^{4}$	$-1.360\ 6591\times10^{4}$	b_{12}	$5.761\ 1507\times10^{6}$	$7.751\ 9414\times10^{7}$
d_2	$1.257\ 4194\times10^{2}$	$2.671\ 0580\times10^{2}$	b_{13}	$-8.161\ 0172\times10^{9}$	$-5.390\ 6536\times10^{10}$
d_3	$-1.273\ 7055\times10^{-1}$	$-2.362\ 4147\times10^{-2}$	b_{14}	$3.401\ 9827\times10^{14}$	$3.834\ 1277\times10^{15}$
d_4	$9.596\ 8764\times10^{-6}$	$-4.524\ 8282\times10^{-5}$	b_{15}	$1.053\ 6524\times10^{22}$	$-1.406\ 1663\times10^{22}$
d_5	$2.539\ 2061\times10^{-9}$	$1.940\ 3623\times10^{-8}$	b_{16}	$3.638\ 6947\times10^{11}$	$-1.074\ 4115\times10^{13}$
d_6	$4.650\ 7610\times10^{0}$	$-2.377\ 7028\times10^{1}$	b_{17}	0	$1.234\ 4220\times10^{16}$
b_1	$-4.090\ 9899\times10^{2}$	$1.770\ 6253\times10^{3}$	b_{18}	0	$-4.554\ 3334\times10^{18}$
b_2	$6.221\ 3928\times10^{5}$	$-1.407\ 2709\times10^{6}$	b_{19}	$-6.955\ 9033\times10^{18}$	$5.352\ 2650\times10^{20}$
b_3	$-4.269\ 9835\times10^{11}$	$2.815\ 5700\times10^{10}$	b_{20}	$-3.696\ 5023\times10^{13}$	$5.120\ 4682\times10^{14}$
b_4	$6.987\ 0832\times10^{15}$	$-1.982\ 3817\times10^{15}$	b_{21}	$1.660\ 5316\times10^{16}$	$-5.953\ 6320\times10^{17}$
b_5	$-6.741\ 6069\times10^{21}$	$-8.976\ 3010\times10^{19}$	b_{22}	0	$2.277\ 0005\times10^{20}$
b_6	$2.827\ 2012\times10^{25}$	$5.317\ 8697\times10^{24}$	b_{23}	0	$-2.835\ 8570\times10^{22}$
b_7	$-2.187\ 7931\times10^{35}$	0	b_{24}	$3.341\ 9911\times10^{5}$	0
b_8	$-6.474\ 1658\times10^{4}$	$-3.783\ 7044\times10^{5}$	b_{25}	$-4.064\ 7594\times10^{8}$	0
b_9	$1.593\ 2143\times10^{8}$	$3.554\ 6610\times10^{8}$	b_{26}	$6.923\ 3929\times10^{13}$	$4.048\ 8404\times10^{12}$
b_{10}	0	$-7.527\ 8673\times10^{10}$	b_{27}	$-1.458\ 5349\times10^{18}$	0
b_{11}	$-2.295\ 1780\times10^{13}$	$-3.711\ 0382\times10^{11}$	γ	$1.944\ 4748\times10^{4}$	$2.479\ 0640\times10^{4}$

should be noted that the comparison with the available data was performed only with those taken into consideration for the establishment of the skeleton tables in the previous work by Date and Iwasaki[1]. The average deviation of these reported experimental data from Eq. (1) are shown in Table 2 and it can be understood that the computed compressibility factor values are in satisfactory agreement with the skeleton table values and the experimental data which were evaluated to be found more reliable by the HPDCJ[1]. The computed compressibility factor values as well as their comparison with the skeleton table values are tabulated for propane and propene in Tables 3 and 4, respectively.

It is confirmed that Eq. (1) can reproduce satisfactorily the skeleton table values of propane and propene for the whole temperature ranges assigned within the gaseous phases. But, simply because of the fact that the derived values with respect to the isobaric specific heat capacity are less reliable along the two bounded isotherms of 298.15 K and 548.15 K for propane, the effective range of the present equation of state for gaseous propane is limited to somewhat narrow region as mentioned previously and therefore those computed values in this limited range of temperature are only given in Table 3. On the other hand, the derived values of the isobaric specific heat capacity for propene are not reasonable only along the isotherm of 373.15 K for supercritical pressures and hence this region is excluded from the effective range of the proposed equation as shown in Table 4, however the P–V–T behavior along this isotherm is completely satisfactory. It may be understood that this kind of behavior is mainly due to the difficulty of fitting the P–V–T plane alone without considering the tendency of the derived property values especially in such a vicinity of the critical isotherm as 373.15 K for gaseous propene.

Table 6-1 Calculated values of molar volume, molar enthalpy and molar entropy for gaseous propane

Pressure	Temperature K (°C)										
MPa	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)	523.15 (250)
0.1	22245	24391	26529	28657	30776	32888	34994	37095	39194	41289	43382
	-1903	-112.8	1805	3855	6033	8332	10750	13290	15940	18700	21570
	-6.115	0.1128	6.285	12.40	18.43	24.40	30.29	36.11	41.86	47.55	53.17
0.5		4533.1	5019.1	5491.2	5951.3	6402.2	6846.5	7286.0	7721.9	8154.9	8585.6
		-608.9	1362	3474	5706	8050	10500	13070	15740	18520	21410
		-14.38	-8.038	-1.745	4.446	10.52	16.50	22.39	28.19	33.92	39.57
1			2308.3	2583.8	2841.9	3088.1	3326.4	3559.2	3787.9	4013.5	4236.7
			723.7	2948	5269	7680	10180	12790	15490	18300	21210
			-15.21	-8.581	-2.143	4.108	10.20	16.18	22.05	27.83	33.53
2				1099.3	1273.0	1424.3	1563.3	1694.7	1821.1	1943.7	2063.5
				1641	4266	6866	9498	12190	14970	17830	20790
				-17.16	-9.874	-3.129	3.282	9.469	15.49	21.39	27.19
3					729.26	861.46	972.24	1072.2	1165.6	1254.6	1340.4
					2976	5923	8745	11560	14430	17360	20370
					-15.92	-8.278	-1.403	5.066	11.28	17.32	23.22
4					415.73	570.69	673.64	760.19	838.20	910.89	979.88
					893.9	4774	7902	10890	13860	16870	19940
					-23.02	-12.93	-5.306	1.545	7.996	14.20	20.21
5						383.73	491.60	572.46	642.11	705.41	764.53
						3256	6944	10160	13260	16360	19500
						-17.93	-8.933	-1.550	5.192	11.58	17.73
6						246.01	368.03	447.20	511.93	569.22	621.86
						1044	5840	9375	12640	15850	19060
						-24.26	-12.55	-4.426	2.673	9.274	15.57
7						173.25	280.27	358.34	419.76	472.81	520.83
						-1028	4597	8542	12000	15330	18620
						-29.98	-16.25	-7.179	0.3410	7.182	13.64
8						148.13	221.17	293.55	351.79	401.48	445.92
						-2053	3368	7681	11350	14800	18180
						-32.95	-19.74	-9.824	-1.851	5.247	11.87
9						136.47	185.81	246.57	300.56	347.11	388.56
						-2612	2388	6845	10700	14270	17740
						-34.71	-22.53	-12.29	-3.914	3.441	10.23
10						129.48	165.19	213.42	261.66	304.87	343.59
						-2970	1694	6101	10070	13750	17300
						-35.94	-24.58	-14.46	-5.829	1.752	8.705
11						124.66	152.28	190.45	232.17	271.69	307.74
	1st line : molar volume V in $cm^3 \cdot mol^{-1}$					-3221	1201	5485	9496	13260	16880
						-36.89	-26.12	-16.28	-7.570	0.1814	7.279
12	2nd line : molar enthalpy H in $J \cdot mol^{-1}$					121.03	143.50	174.36	209.88	245.46	278.84
	3rd line : molar entropy S in $J \cdot K^{-1} \cdot mol^{-1}$					-3406	837.7	4995	8985	12800	16480
						-37.67	-27.33	-17.78	-9.116	-1.267	5.948
13						118.16	137.09	162.73	192.97	224.65	255.32
						-3548	560.3	4606	8547	12370	16100
						-38.32	-28.32	-19.03	-10.47	-2.588	4.710
14						115.80	132.16	154.00	179.98	208.05	236.07
						-3659	342.5	4294	8176	11990	15740
						-38.90	-29.15	-20.07	-11.64	-3.782	3.564
15						113.80	128.23	147.21	169.81	194.70	220.20
						-3746	168.1	4041	7865	11660	15420
						-39.40	-29.87	-20.97	-12.67	-4.857	2.507
16						112.07	124.99	141.76	161.69	183.86	207.04
						-3815	26.34	3833	7603	11370	15120
						-39.86	-30.50	-21.76	-13.57	-5.823	1.536

Table 6-2 (continued)

Pressure	Temperature K (°C)					
MPa	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)	523.15 (250)
17	110.55	122.25	137.28	155.06	174.95	196.03
	-3869	-89.94	3660	7382	11110	14860
	-40.28	-31.07	-22.46	-14.38	-6.694	0.6451
18	109.19	119.90	133.51	149.55	167.52	186.76
	-3911	-185.9	3514	7193	10890	14620
	-40.66	-31.58	-23.09	-15.10	-7.481	-0.1729
19	107.98	117.85	130.29	144.89	161.25	178.87
	-3943	-265.2	3391	7032	10700	14410
	-41.01	-32.05	-23.66	-15.75	-8.197	-0.9250
20	106.87	116.03	127.49	140.89	155.88	172.10
	-3966	-330.8	3285	6893	10530	14220
	-41.34	-32.48	-24.13	-16.34	-8.851	-1.618
25	102.51	109.26	117.50	126.99	137.55	148.98
	-3989	-512.8	2956	6433	9957	13560
	-42.71	-34.24	-26.28	-18.73	-11.47	-4.417
30					126.64	
					9654	
					-13.40	

1st line : molar volume V in $cm^3 \cdot mol^{-1}$

2nd line : molar enthalpy H in $J \cdot mol^{-1}$

3rd line : molar entropy S in $J \cdot K^{-1} \cdot mol^{-1}$

Basic Correlating Function

When density and temperature are chosen as the independent variables, the expressions for pressure and all other thermodynamic properties can be derived directly by the partial differentiation of a basic correlating function $A=A(\rho, T)$, where A is the molar Helmholtz function. In the present study, the molar Helmholtz function A in $J \cdot mol^{-1}$ is derived from Eqs. (1) and (2) as follows:

$$\begin{aligned} A=&d_1+d_2T+d_3T^2+d_4T^3+d_5T^4+d_6T\cdot\ln T+RT\cdot\ln\rho \\ &+(b_1T+b_2+b_3/T^2+b_4/T^4+b_5/T^6+b_6/T^8+b_7/T^{12})\rho \\ &+(b_8T+b_9+b_{10}/T+b_{11}/T^2)\rho^2+(b_{12}T+b_{13}+b_{14}/T^2+b_{15}/T^5)\rho^3 \\ &+(b_{16}+b_{17}/T+b_{18}/T^2+b_{19}/T^3)\rho^4 \\ &+(b_{20}+b_{21}/T+b_{22}/T^2+b_{23}/T^3)\rho^5 \\ &+(b_{24}T+b_{25}+b_{26}/T^2+b_{27}/T^4)[1/\gamma-(\rho^2/2+1/\gamma)\exp(-\gamma\rho^2)]. \end{aligned} \quad (3)$$

The numerical constants in Eq. (3) are given in Table 5. The numerical values of d_1 and d_2 in Eq. (3) are fixed due to the following specified conditions:

(i) Molar entropy, $S=0$ $J \cdot K^{-1} mol^{-1}$ at 298.15 K and 0.101325 MPa,

(ii) Molar enthalpy, $H=0$ $J \cdot mol^{-1}$ at 298.15 K and 0 MPa.

Derived Functions

Table 7-1 Calculated values of molar volume, molar enthalpy and molar entropy for gaseous propene

Pressure	Temperature K (°C)										
MPa	248.15 (-25)	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
0.1	20110	22286	24439	26574	28697	30810	32917	35019	37118	39215	41310
	-3179	-1691	-110.4	1558	3315	5164	7105	9140	11270	13490	15800
	-11.13	-5.423	0.1129	5.485	10.72	15.85	20.88	25.84	30.72	35.55	40.31
0.5			4586.6	5067.9	5532.1	5985.3	6431.2	6871.9	7309.0	7743.2	8175.3
			-590.7	1168	2989	4884	6860	8921	11070	13310	15640
			-14.40	-8.734	-3.305	1.950	7.073	12.09	17.03	21.89	26.68
1			2071.9	2362.7	2627.3	2877.1	3117.6	3352.0	3582.0	3808.9	4033.4
			-1312	615.6	2545	4512	6540	8640	10820	13080	15430
			-21.93	-15.72	-9.969	-4.512	0.7458	5.860	10.86	15.77	20.61
2				959.63	1153.1	1312.1	1455.2	1589.1	1717.2	1841.3	1962.5
				-878.0	1478	3673	5843	8042	10290	12610	15010
				-25.02	-17.99	-11.90	-6.273	-0.9174	4.253	9.287	14.21
3					623.07	776.45	894.82	998.65	1094.4	1185.1	1272.3
					-69.11	2645	5053	7393	9740	12130	14570
					-24.90	-17.37	-11.12	-5.417	-0.0279	5.156	10.19
4						489.29	608.35	700.99	782.19	856.89	927.41
						1258	4129	6880	9152	11620	14130
						-22.75	-15.29	-9.078	-3.400	1.968	7.130
5							429.50	520.33	594.32	660.07	720.87
							3004	5888	8528	11100	13680
							-19.41	-12.38	-6.314	-0.7214	4.588
6							302.88	398.37	468.93	529.17	583.66
							1562	5003	7864	10560	13220
							-23.94	-15.54	-8.973	-3.109	2.369
7							211.82	310.99	379.74	436.24	486.27
							-227.4	4021	7163	10010	12760
							-29.07	-18.70	-11.48	-5.297	0.3698
8							162.72	247.70	313.93	367.40	413.97
							-1725	2980	6436	9444	12290
							-33.30	-21.81	-13.87	-7.337	-1.466
9							141.27	203.88	264.69	315.02	358.62
							-2587	1989	5706	8878	11830
							-35.84	-24.69	-16.14	-9.253	-3.172
10							130.13	175.39	227.98	274.56	315.33
							-3101	1166	5008	8322	11370
							-37.47	-27.08	-18.25	-11.05	-4.765
11							123.16	157.14	200.91	243.09	280.96
							-3444	537.7	4377	7791	10930
	1st line : molar volume V in $cm^3 \cdot mol^{-1}$						-38.65	-28.95	-20.13	-12.72	-6.253
12	2nd line : molar enthalpy H in $J \cdot mol^{-1}$						118.26	145.03	181.06	218.51	253.40
	3rd line : molar entropy S in $J \cdot K^{-1} \cdot mol^{-1}$						-3693	68.30	3833	7298	10500
							-39.58	-30.42	-21.77	-14.25	-7.639
13							114.53	136.53	166.39	199.26	231.13
							-3882	-287.2	3379	6852	10110
							-40.34	-31.59	-23.17	-15.63	-8.924
14							111.56	130.24	155.37	184.08	213.01
							-4031	-562.9	3004	6457	9738
							-41.00	-32.56	-24.37	-16.87	-10.11
15							109.10	125.36	146.89	172.02	198.17
							-4151	-781.8	2696	6113	9402
							-41.58	-33.38	-25.39	-17.97	-11.20
16							107.20	121.44	140.20	162.32	185.92
							-4249	-958.9	2441	5815	9098
							-42.10	-34.09	-26.28	-18.95	-12.19

Table 7-2 (continued)

Pressure	Temperature K (°C)				
MPa	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
17	105.21 -4331 -42.57	118.21 -1104 -34.71	134.80 2230 -27.06	154.42 5558 -19.83	175.74 8827 -13.10
18	103.62 -4399 -43.00	115.47 -1226 -35.28	130.34 2053 -27.75	147.90 5337 -20.62	167.21 8585 -13.93
19	102.21 -4455 -43.40	113.11 -1327 -35.79	126.59 1904 -28.37	142.43 5147 -21.32	159.99 8371 -14.69
20	100.93 -4502 -43.78	111.05 -1413 -36.25	123.39 1777 -28.93	137.79 4984 -21.97	153.83 8181 -15.38
25	95.997 -4639 -45.35	103.56 -1683 -38.16			
30	92.502 -4670 -46.62	98.643 -1795 -39.61			
35	89.814 -4638 -47.68	95.040 -1819 -40.81			
40	87.640 -4564 -48.61	92.222 -1786 -41.84			
45	85.820 -4459 -49.43	89.920 -1715 -42.75			
50	84.258 -4331 -50.18	87.982 -1616 -43.57			
60	81.680 -4026 -51.49	84.851 -1359 -45.00			

1st line : molar volume V in $cm^3 \cdot mol^{-1}$
2nd line : molar enthalpy H in $J \cdot mol^{-1}$
3rd line : molar entropy S in $J \cdot K^{-1} \cdot mol^{-1}$

According to the general thermodynamic relations, the pressure P in MPa, the molar entropy S in $J \cdot K^{-1} mol^{-1}$, the molar enthalpy H in $J \cdot mol^{-1}$, the molar isobaric specific heat capacity C_p in $J \cdot K^{-1} mol^{-1}$ and the molar isochoric specific heat capacity C_v in $J \cdot K^{-1} mol^{-1}$ can be calculated by the following expressions:

$$P=\rho^2(\partial A/\partial\rho)_T\,, \tag{4}$$

$$S=-(\partial A/\partial T)_\rho\,, \tag{5}$$

$$H=A-T(\partial A/\partial T)_\rho+\rho(\partial A/\partial\rho)_T\,, \tag{6}$$

$$C_p=T\left[-(\partial^2 A/\partial T^2)_\rho+\frac{\rho(\partial^2 A/\partial\rho\partial T)^2}{2(\partial A/\partial\rho)_T+\rho(\partial^2 A/\partial\rho^2)_T}\right], \tag{7}$$

$$C_v=-T(\partial^2 A/\partial T^2)_\rho\,. \tag{8}$$

In addition, the compressibility factor Z and the molar volume V in $cm^3 \cdot mol^{-1}$ can be calculated from the following expressions, respectively:

$$Z=P/RT\rho\,, \tag{9}$$

$$V=1/\rho\,. \tag{10}$$

Calculated Thermodynamic Properties

By differentiating the new equations of state expressed in the basic correlating functions for gaseous propane and propene, Eq. (3), all of the thermodynamic properties may be calculated as shown in the previous section. The calculated molar volume, the molar enthalpy and the molar entropy for both gaseous propane and propene are tabulated in Tables 6 and 7, respectively.

With respect to the molar isobaric specific heat capacity for both propane and propene, the calculated results are shown on C_p—ρ diagrams in Figs. 3 and 4. It is also noteworthy that the calculated C_p values for gaseous propene are in good agreement with the reported experimental data by Bier *et al.*[8], where they overlap. The average deviation is found as 0.362% with respect to 96 data points compared.

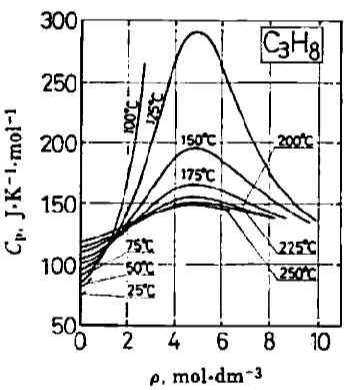

Fig. 3 Calculated molar isobaric specific heat capacity for propane

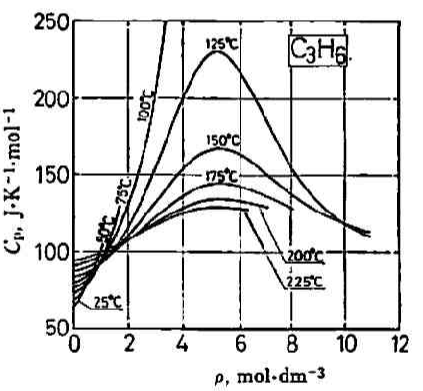

Fig. 4 Calculated molar isobaric specific heat capacity for propene

Conclusion

As a part of the activities of the High Pressure Data Center of Japan, new equations of state, Eq. (1), for both gaseous propane and propene are formulated based upon the most probable and additional recommended compressibility factor values proposed previously by the HPDCJ. The present formulations given as a function of the density and temperature can cover the range of temperature 273.15 K–523.15 K and pressures up to 30 MPa for propane, and also that of temperature 248.15 K–498.15 K and pressures up to 60 MPa for propene, respectively.

Based upon the established equations of state, the basic correlating functions given as the molar Helmholtz function are derived and hence the additional thermodynamic property values such as molar volume, molar entropy, molar enthalpy and molar isobaric specific heat capacity, are also calculated and presented.

It was also confirmed that the so-called extended BWR equations are very effective to cover the wide range of the state parameters in gaseous region especially for the serial hydrocarbons like ethane, ethene, propane and propene in the previous and present studies by the present authors.

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