EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF 1,1,1,2-TETRAFLUOROETHANE (REFRIGERANT R134a)

E. T. Vas'kov

UDC 621.564:536.71

An equation of state and tables of thermodynamic properties of R134a in the saturation state and in the one-phase region are obtained in the temperature interval 320–500 K at pressures ranging from 0.01 to 7.5 MPa.

Using experimental data on p, ρ, T an equation of state has been constructed in virial form and used to compose tables of thermodynamic properties of refrigerant R134a in the one-phase region (T = 300–500 K, p = 0.01–7.5 MPa) and on the liquid-vapor equilibrium line.

The Basic Physical Properties of the Refrigerant R134a (CH_2F-CF_3).

Kilomole mass μ = 103.031 kg/kmole.

Boiling temperature at the pressure p = 0.101325 MPa, T_b = 247.0 K.

Critical parameters: temperature T_{cr} = 374.34 K, pressure p_{cr} = 4.066 MPa, density ρ_{cr} = 514.0 kg/m^3.

Triple point temperature T_{tr} = 172 K.

Gas constant R = 81.4882 J/(kg·K).

A new cooling agent R134a is recommended as an ozone-nondestructive working medium for refrigerating and heat pump installations instead of the ozone-active refrigerant R12. Tetrafluoroethane may be used as a cooling agent, a propellant, and a raw material for fluoroorganic synthesis [1]. Thermodynamic properties of R134a that are needed for designing thermal processes and heat exchangers of refrigerating machines and heat pumps have been studied insufficiently fully.

Using experimental data on p, ρ, T obtained by Basu and Wilson [2] (T = 314–448 K, p = 1–6.7 MPa, ρ = 51–521), Weber [3] (T = 313–423 K, p = 0.3–5.3 MPa, ρ = 10–233 kg/m^3), and P. M. Kessel'man, V. P. Zheleznyi, Yu. V. Semenyuk [4] (T = 213–368 K, p = 0.3–20 MPa, ρ = 980–1476 kg/m^3) and on heat capacity, we have derived an equation of state in virial form and a system of equations for determination of thermodynamic properties of gases and liquids and used them to calculate thermodynamic tables for the refrigerant R134a that contain a substantially larger set of quantities than those published earlier.

The equation of state in virial form is as follows:

$$z = p/\rho RT = \sum_{i=1}^{m} \sum_{j=0}^{S_i} b_{ij} \frac{w^i}{\tau^j}, \tag{1}$$

where the reduced temperature and density are $\tau = T/T_{cr}$, $w = \rho/\rho_{cr}$, T_{cr} = 374.34 K, ρ_{cr} = 514.00 kg/m^3, and R = 81.4882 J/(kg·K). The coefficients b_{ij} of the equation of state are determined by the least-squares method:

$b_{10} = -0.781492558 \cdot 10^{-1}$ $\quad b_{20} = 0.446092073$

$b_{11} = -0.495166767$ $\quad b_{21} = 0.487600723 \cdot 10^{-1}$

$b_{12} = -0.512530720$ $\quad b_{22} = -0.282865108 \cdot 10^{-1}$

$b_{13} = -0.286105987$ $\quad b_{23} = 0.301319490 \cdot 10^{-1}$

$b_{14} = -0.186848142 \cdot 10^{-1}$ $\quad b_{24} = 0.666366435 \cdot 10^{-1}$

$b_{15} = 0.468269570 \cdot 10^{-1}$ $\quad b_{25} = 0.364932303 \cdot 10^{-2}$

St. Petersburg State University of Architecture and Civil Engineering, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 1, pp. 66-70, January-February, 1995. Original article submitted July 20, 1993.

TABLE 1. Thermodynamic Properties of Refrigerant R134a in the Saturation State

T, K	p, MPa	ρ'	ρ''	h'	h''	r	s'	s''
		kg/m^3		kJ/kg			kJ/(kg·K)	
320	1,216	1117	60,56	367,4	519,3	151,9	0,4198	0,8957
322	1,280	1108	64,02	370,4	520,2	149,8	0,4293	0,8955
324	1,346	1098	67,66	373,3	520,9	147,6	0,4387	0,8952
326	1,414	1089	71,51	376,3	521,6	145,4	0,4482	0,8949
328	1,485	1079	75,57	379,3	522,3	143,0	0,4578	0,8946
330	1,559	1070	79,86	382,4	523,0	140,6	0,4673	0,8942
332	1,636	1059	84,80	385,5	523,6	138,1	0,4770	0,8938
334	1,715	1049	89,20	388,6	524,2	135,6	0,4867	0,8932
336	1,797	1038	94,29	391,8	524,7	132,9	0,4964	0,8926
338	1,882	1027	99,70	395,0	525,2	130,2	0,5062	0,8919
340	1,971	1016	105,4	398,3	525,6	127,3	0,5162	0,8910
342	2,062	1004	111,6	401,6	526,0	124,3	0,5262	0,8901
344	2,156	991,4	118,1	405,1	526,2	121,2	0,5363	0,8890
346	2,254	978,6	125,1	408,5	526,4	117,9	0,5465	0,8877
348	2,355	965,3	132,7	412,1	526,5	114,5	0,5569	0,8862
350	2,460	951,3	140,8	415,7	526,6	110,9	0,5675	0,8846
352	2,568	936,7	149,6	419,4	526,5	107,1	0,5782	0,8826
354	2,680	921,4	159,2	423,2	526,2	103,0	0,5891	0,8804
356	2,796	905,3	169,7	427,1	525,9	98,76	0,6002	0,8778
358	2,916	888,3	181,2	431,1	525,3	94,20	0,6115	0,8748
360	3,040	870,2	194,1	435,3	524,6	89,31	0,6231	0,8714
362	3,168	851,0	208,6	439,6	523,6	84,02	0,6350	0,8673
364	3,300	830,3	225,0	444,0	522,3	78,27	0,6473	0,8624
366	3,437	807,7	244,1	448,6	520,6	71,93	0,6600	0,8566
368	3,579	782,8	266,7	453,5	518,4	64,85	0,6733	0,8496
370	3,727	754,5	294,0	458,3	515,6	56,79	0,6875	0,8411
371	3,802	738,4	309,9	461,6	513,9	52,30	0,6950	0,8361
372	3,879	720,4	327,6	464,7	512,1	47,43	0,7031	0,8307
373	3,958	697,3	349,3	468,2	509,7	41,51	0,7126	0,8239
374	4,038	585,5	400,8	480,8	503,1	22,25	0,7461	0,8055

$b_{30} = 0.127873626$
$b_{31} = -0.187767241$
$b_{32} = -0.126873960$
$b_{33} = 0.491821934 \cdot 10^{-1}$
$b_{34} = 0.153441180$
$b_{35} = 0.127385408$

$b_{40} = 0.188857157 \cdot 10^{-1}$
$b_{41} = -0.283721720$
$b_{42} = -0.139456353$
$b_{43} = 0.796697958 \cdot 10^{-1}$
$b_{44} = 0.171108358$
$b_{45} = 0.132397745$

$b_{50} = 0.120450558$
$b_{51} = -0.214873294$
$b_{52} = -0.457511318 \cdot 10^{-1}$
$b_{53} = 0.110188081$
$b_{54} = 0.844099155 \cdot 10^{-1}$
$b_{55} = -0.245654666 \cdot 10^{-1}$

$b_{60} = 0.206041163$
$b_{61} = -0.132270102$
$b_{62} = 0.433624884 \cdot 10^{-1}$
$b_{63} = 0.599824251 \cdot 10^{-1}$
$b_{64} = -0.961749419 \cdot 10^{-1}$
$b_{65} = -0.215275620$

$b_{70} = 0.103994087$
$b_{71} = -0.100175413$
$b_{72} = 0.109170506$
$b_{73} = -0.317313717 \cdot 10^{-1}$
$b_{74} = -0.163704737$
$b_{75} = -0.131246201$

$b_{80} = -0.101373353$
$b_{81} = -0.123978345 \cdot 10^{-1}$
$b_{82} = 0.214692570$
$b_{83} = -0.758203451 \cdot 10^{-1}$
$b_{84} = 0.102462073$
$b_{85} = 0.271199782$

$b_{90} = -0.111154847$
$b_{91} = 0.104906664$
$b_{92} = 0.124500694$
$b_{93} = -0.35117919$
$b_{94} = 0.177978707$
$b_{95} = -0.140212794$

$b_{10,0} = 0.852222580 \cdot 10^{-1}$
$b_{10,1} = -0.146504292$
$b_{10,2} = 0.600819801 \cdot 10^{-1}$
$b_{10,3} = 0.565724755 \cdot 10^{-1}$
$b_{10,4} = -0.464953078 \cdot 10^{-1}$
$b_{10,5} = 0.222758524 \cdot 10^{-1}$

TABLE 2. Thermodynamic Properties of Refrigerant R134a in the Saturation State

T, K	a′	a″	μ′	μ″	k′	k″	f′=f″	α′	α″	γ′	γ″·10²
	m/sec		K/MPa		—		MPa	1/K			
320	412,3	137,8	0,2215	21,16	156,1	0,9454	0,9980	4,259	7,894	0,3975	0,5662
322	404,6	137,0	0,2540	20,94	141,7	0,9385	1,043	4,402	8,152	0,3694	0,5747
324	396,7	136,1	0,2892	20,72	128,5	0,9313	1,089	4,558	8,432	0,3433	0,5836
326	388,7	135,2	0,3272	20,52	116,3	0,9240	1,137	4,728	8,738	0,3189	0,5931
328	380,5	134,2	0,3684	20,33	105,2	0,9164	1,185	4,915	9,072	0,2963	0,6032
330	372,1	133,2	0,4130	20,15	94,98	0,9087	1,235	5,121	9,489	0,2752	0,6140
332	363,6	132,1	0,4615	19,99	85,62	0,9007	1,287	5,348	9,844	0,2556	0,6254
334	355,0	131,0	0,5141	19,83	77,06	0,8925	1,339	5,559	10,29	0,2374	0,6376
336	346,2	129,8	0,5715	19,69	69,22	0,8842	1,393	5,877	10,79	0,2203	0,6507
338	337,2	128,6	0,6340	19,56	62,05	0,8756	1,448	6,185	11,35	0,2044	0,6646
340	328,1	127,3	0,7022	19,44	55,50	0,8669	1,504	6,529	11,97	0,1895	0,6796
342	318,9	125,9	0,7770	19,33	49,50	0,8579	1,562	6,914	12,68	0,1755	0,6958
344	309,4	124,5	0,8991	19,23	44,02	0,8489	1,620	7,346	13,49	0,1624	0,7133
346	299,8	123,0	0,9496	19,14	39,01	0,8397	1,680	7,835	14,42	0,1501	0,7322
348	289,8	121,4	1,050	19,06	34,43	0,8304	1,742	8,389	15,49	0,1384	0,7527
350	279,6	119,8	1,161	18,98	30,24	0,8210	1,804	9,025	16,75	0,1275	0,7752
352	269,1	118,1	1,287	18,91	26,42	0,8117	1,868	9,759	18,25	0,1171	0,7998
354	258,3	116,2	1,428	18,83	22,93	0,8026	1,932	10,62	20,05	0,1073	0,8270
356	247,0	114,4	1,590	18,76	9,76	0,7937	1,999	11,64	22,25	0,09795	0,8572
358	235,3	112,4	1,777	18,67	16,87	0,7853	2,066	12,87	25,00	0,08909	0,8910
360	223,1	110,4	1,997	18,56	14,25	0,7777	2,134	14,39	28,51	0,0867	0,9291
362	210,4	108,2	2,260	18,42	11,89	0,7713	2,204	16,34	33,12	0,7266	0,9726
364	197,0	106,0	2,581	18,23	9,764	0,7667	2,274	18,92	39,38	0,06503	1,023
366	183,0	103,8	2,983	17,95	7,868	0,7650	2,346	22,53	48,22	0,05776	1,081
368	168,2	101,5	3,506	17,54	6,186	0,7677	2,419	27,98	61,24	0,05082	1,150
370	152,4	99,24	4,220	16,94	4,704	0,7771	2,493	37,32	81,13	0,04414	1,232
371	144,1	98,15	4,689	16,55	4,031	0,7852	2,531	45,07	94,77	0,04087	1,279
372	135,3	97,09	5,274	16,09	3,399	0,7961	2,569	57,35	111,4	0,03760	1,329
373	124,8	95,91	6,138	15,53	2,748	0,8113	2,607	84,58	135,2	0,03406	1,391
374	90,78	92,87	11,50	14,51	1,195	0,8504	2,649	251,8	244,5	0,02346	1,551

TABLE 3. Thermodynamic Properties of Refrigerant R134a in the One-Phase Region on the Isotherm $T = 320$ K

p, MPa	ρ, kg/m^3	z	h, kJ/kg	s	c_V	c_p
				kJ/(kg·K)	J/(kg·K)	
0.01	0.3841	0.9985	541.9	1.341	811.6	893.8
0.1	3.895	0.9845	540.5	1.150	817.1	905.7
0.2	7.918	0.9687	539.0	1.090	823.4	919.9
0.3	12.08	0.9523	537,4	1.053	829.9	935.3
0.4	16.40	0.9355	535.8	1.026	836.7	951.9
0.5	20.88	0.9181	534.1	1.004	843.6	970.1
0.6	25.56	0.9002	532.3	0.9848	850.8	990.2
0.7	30.45	0.8815	530.5	0.9679	858.3	1012
0.8	35.59	0,8621	528.5	0.9524	866.1	1037
0.9	41.00	0.8418	526.5	0.9379	874.3	1066
1.0	46.74	0.8205	524.4	0.9242	883.0	1098
1.5	1119	0.05139	367.3	0.4187	881.7	1460
2.0	1124	0.06823	367.2	0.4169	888.5	1448
2.5	1129	0.08493	367.1	0.4151	894.7	1437
3.0	1133	0.1015	367.0	0.4134	900.5	1427
3.5	1138	0.1180	366.9	0.4117	905.8	1417
4.0	1142	0.1343	366.8	0.4101	910.6	1408
4.5	1147	0.1505	366.8	0.4085	915.0	1400
5.0	1151	0.1666	366.7	0.4069	919.0	1393
5.5	1155	0.1826	366.6	0.4054	922.5	1386
6.0	1159	0.1986	366.6	0.4040	925.6	1380
6.5	1163	0.2144	366.5	0.4025	928.3	1374
7.0	1167	0.2301	366.5	0.4011	930.6	1368
7.5	1170	0.2457	366.5	0.3998	932.5	1363

TABLE 4. Thermodynamic Properties of R134a in the One-Phase Region (the Isotherm $T = 320$ K)

p, MPa	a, m/sec	μ, K/MPa	h	f, MPa	α	γ
					1/K	
0.01	169.2	16.55	1.100	0.009985	3.143	0.003138
0.1	167.4	16.75	1.091	0.09848	3.310	0.003258
0.2	165.3	17.00	1.081	0.1939	3.512	0.003399
0.3	163.1	17.26	1.071	0.2863	3.734	0.003549
0.4	160.8	17.54	1.060	0.3757	3.980	0.003709
0.5	158.5	17.84	1.049	0.4620	4.255	0.003881
0.6	156.0	18.17	1.037	0.5454	4.562	0.004066
0.7	153.5	18.53	1.025	0.6257	4.910	0.004266
0.8	150.8	18.93	1.012	0.7029	5.309	0.004484
0.9	148.0	19.37	0.9975	0.7772	5.770	0.004722
1.0	145.0	19.86	0.9824	0.8483	6.311	0.004984
1.5	413.2	0.2082	127.4	1.014	4.189	0.3222
2.0	414.7	0.1859	96.68	1.032	4.071	0.2415
2.5	416.4	0.1650	78.30	1.049	3.961	0.1931
3.0	418.2	0.1452	66.08	1.067	3.858	0.1610
3.5	420.2	0.1265	57.41	1.086	3.762	0.1381
4.0	422.4	0.1088	50.94	1.104	3.672	0.1209
4.5	424.7	0.09205	45.95	1.123	3.587	0.1077
5.0	427.2	0.07617	42.00	1.142	3.506	0.09718
5.5	429.9	0.06110	38.81	1.161	3.431	0.08863
6.0	432.9	0.04680	36.19	1.180	3.359	0.08157
6.5	436.1	0.03321	34.02	1.200	3.291	0.07565
7.0	439.5	0.02030	32.19	1.220	3.226	0.07064
7.5	443.1	0.08019	30.65	1.240	3.165	0.06635

The root-mean-square deviation between calculated and experimental data [2-4] and values of ρ is 0.13%, the discrepancy for c_p^0 [2] is 0.05%, the relative error for c_p [5] does not exceed 3–5%, and that for h [6] and s [6] 2%.

The heat capacity of the ideal gas in the temperature range 125–500 K is determined by the equation [2]

$$c_p^0 = -0.5257455 \cdot 10^{-2} + 0.32966570 \cdot 10^{-2} T -$$

$$- 2.017321 \cdot 10^{-6} T^2 + 15.82170 T^{-1} \text{ kJ/(kg·K)}. \tag{2}$$

The data on properties of R134a are correlated in [7–9], the thermodynamic tables are published in [1, 6, 9–11], heat capacity at constant pressure in [5, 12, 13], and liquid molar volume in [14].

NOTATION

T, absolute temperature; p, absolute pressure, ρ, density; z, compressibility factor; p_{cr}, ρ_{cr}, T_{cr}, critical parameters; $\tau = T/T_{cr}$, reduced temperature, $w = \rho/\rho_{cr}$, reduced density; R, gas constant; c_v and c_p, heat capacity at constant volume and at constant pressure, respectively; h, enthalpy; s, entropy; r, D, heat of vaporization; a, velocity of sound; μ, throttling coefficient; k, adiabatic exponent; f, D, volatility; α, coefficient of thermal expansion, K^{-1}; $\alpha = 1/v(\partial v/\partial T)$; γ, thermal coefficient of pressure, K^{-1}; $\gamma = 1/p(\partial p/\partial T)$. Indices: ′ on the boiling line; ″ on the dry vapor line; ^{0}, ideal gas.

REFERENCES

1. B. N. Maksimov, V. G. Baranov, I. L. Serushkin, et al., Industrial Fluoroorganic Products [in Russian], Handbook, Leningrad (1990).
2. D. P. Wilson and R. C. Basu, ASHRAE Transact., Vol. 94, Pt. 2 (1988), p. 2095.
3. L. A. Veber, Int. J. Thermophysics, **10**, No. 3, 617-628 (1989).
4. P. M. Kessel'man, V. P. Zheleznyi, and Yu. V. Semenyuk, Kholod. Tekh., No. 7, 9-11 (1991).
5. A. Salton, S. Nakagava, H. Sato, and K. Watanabe, J. Chem. Eng. Data, **35**, 107-110 (1990).
6. H. Lippold, Lüft- und Kältetechnik, No. 4, 182-185 (1989).
7. M. O. McLinden, Int. J. Refr., **13**, No. 3, 149-162 (1990).
8. A. V. Dobrokhotov, A. V. Maslennikov, E. E. Semenyuk, and E. E. Ustyuzhanin, Kholod. Tekh., No. 7, 16-20 (1991).
9. M. O. McLinden, J. S. Gallagher, L. A. Weber, et al., ASHRAE Transact., No. 4, 3282-3299 (1989).
10. G. Ya. Ruvinskii, G. K. Lavrenchenko, and S. V. Il'yushenko, Kholod. Tekh., No. 7, 20-26 (1990).
11. O. B. Tsvetkov and Yu. A. Laptev, Calculation Methods for the Transfer Properties of Cooling Agents [in Russian], Leningrad (1990).
12. O. P. Ponomareva and N. A. Rusanovskaya, "Experimental studies of the heat capacity at constant pressure of refrigerant R134a," Preprint No. 291-UK91, Deposited at Ukr. NIINTI 06.03.91, Odessa (1991).
13. S. S. Chen, A. S. Rodgers, J. Chao, et al., J. Phys. Ref. Data, **4**, No. 2, 441-456 (1975).
14. K. Ström and U. Gren, J. Chem. Eng. Data, **38**, No. 1, 18-22 (1993).