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Vapor Pressures of New Fluorocarbons

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The vapor pressures of four fluorocarbons have been measured at the following temperature ranges: R123 (2,2-dichloro-1,1,1-trifluoroethane), 273–457 K; R123a (1,2-dichloro-1,1,2-trifluoroethane), 303–458 K; R134a (1,1,1,2-tetrafluoroethane), 253–373 K; and R132b (1,2-dichloro-1,1-difluoroethane), 273–398 K. Determinations of the vapor pressure were carried out by a constant-volume apparatus with an uncertainty of less than 1.0%. The vapor pressures of R123 and R123a are very similar to those of R11 over the whole experimental temperature range, but the vapor pressures of R134a and R132b differ somewhat from those of R12 and R113, respectively, as the temperature increases. The numerical vapor pressure data can be fitted by an empirical equation using the Chebyshev polynomial with a mean deviation of less than 0.3%.

KEY WORDS: R123 ($CHCl_2CF_3$); R123a ($CHClFCClF_2$); R134a (CF_3CH_2F); R132b ($CClF_2CH_2Cl$); saturated vapor pressure; vapor pressure correlation.

1. INTRODUCTION

Various chlorofluorocarbons have been used widely as refrigerants, blowing agents, propellants, and cleaning solvents, because of their excellent natures such as chemical stability, nonflammability, and non-toxicity. In recent years, it has become clear that the compounds containing no hydrogen atoms in their molecules have long atmospheric resistance times and are decomposed by photodecomposition in the stratosphere. This process has serious environmental consequences through the release of chlorine atoms, which act as a chain catalyst of ozone removal reactions. Since the ozone depletion hypothesis was proposed in 1974, it became an urgent problem to develop the alternatives to suspect chlorofluorocarbons, especially R11, R12, and R113.

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As a part of study of the thermodynamic and transport properties of new candidates of the alternatives, the vapor pressures of R123, R123a, R134a, and R132b in the temperature range from 253 to 458 K have been measured in this work.

2. EXPERIMENTAL

The sample fluids, R123, R123a, R134a, and R132b, were synthesized and purified specially by Daikin Industries, Ltd. Their purities are better than 99.9 mol%.

Determinations of the vapor pressure were carried out with a constant-volume apparatus shown schematically in Fig. 1. The sample fluid was introduced into a 304 SS cell or a borosilicate–glass cell (A) and degassed thoroughly by several freeze–pump–thaw cycles. The cell was placed in a constant-temperature liquid bath (B) whose temperature was thermostatically controlled within 10 mK. The temperature was measured by a digital quartz thermometer with an uncertainty of less than 50 mK. When the temperature of the sample is above the room temperature, it is necessary to prevent the condensation of the sample vapor in the pressure measurement system which is located outside the bath (B). Therefore, the

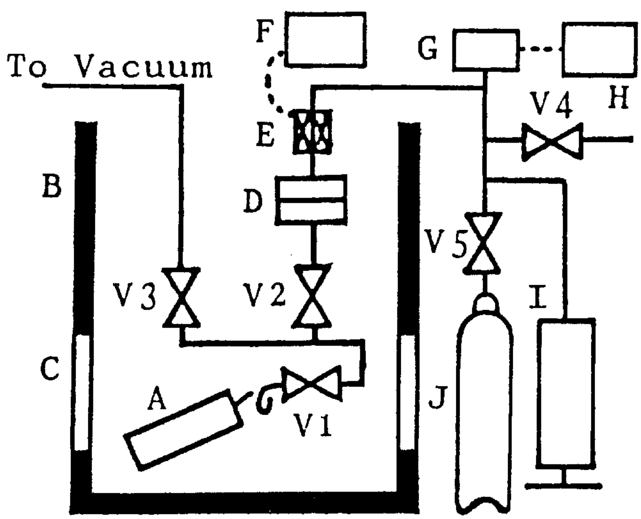

Fig. 1. Schematic diagram of experimental apparatus. A: Sample cell. B: Constant-temperature bath. C: Window. D: Diaphragm cell. E: Differential transformer. F: Null indicator. G: Pressure transducer. H: Pressure indicator. I: Screw pump. J: Air cylinder. V: Valve.

sample vapor and pressure-transmitting fluid in the pressure measurement system were separated from each other by the diaphragm differential-pressure indicator (D), whose sensitivity was less than ±0.5 kPa. The pressure was measured by two types of pressure gauges (G). One is a strain gauge-type digital vacuum gauge (range, 0 to 101.3 kPa) calibrated by the

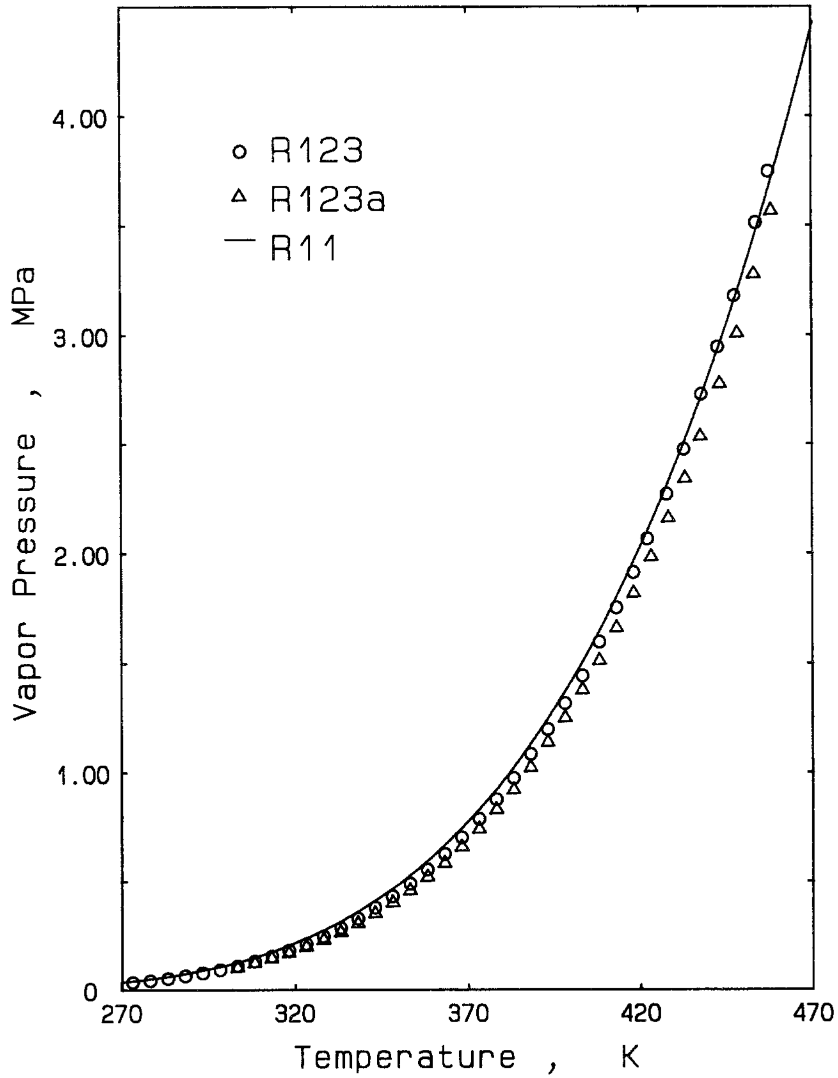

Fig. 2. Vapor pressures of R123, R123a, and R11.

maker to within 0.3 kPa. The other is a digital quartz-pressure gauge (range, 0 to 6.2 MPa) calibrated against a deadweight gauge to within 1.2 kPa. Total uncertainty in the vapor pressure measurements including errors which result from temperature measurements is estimated to be less than 1.0%.

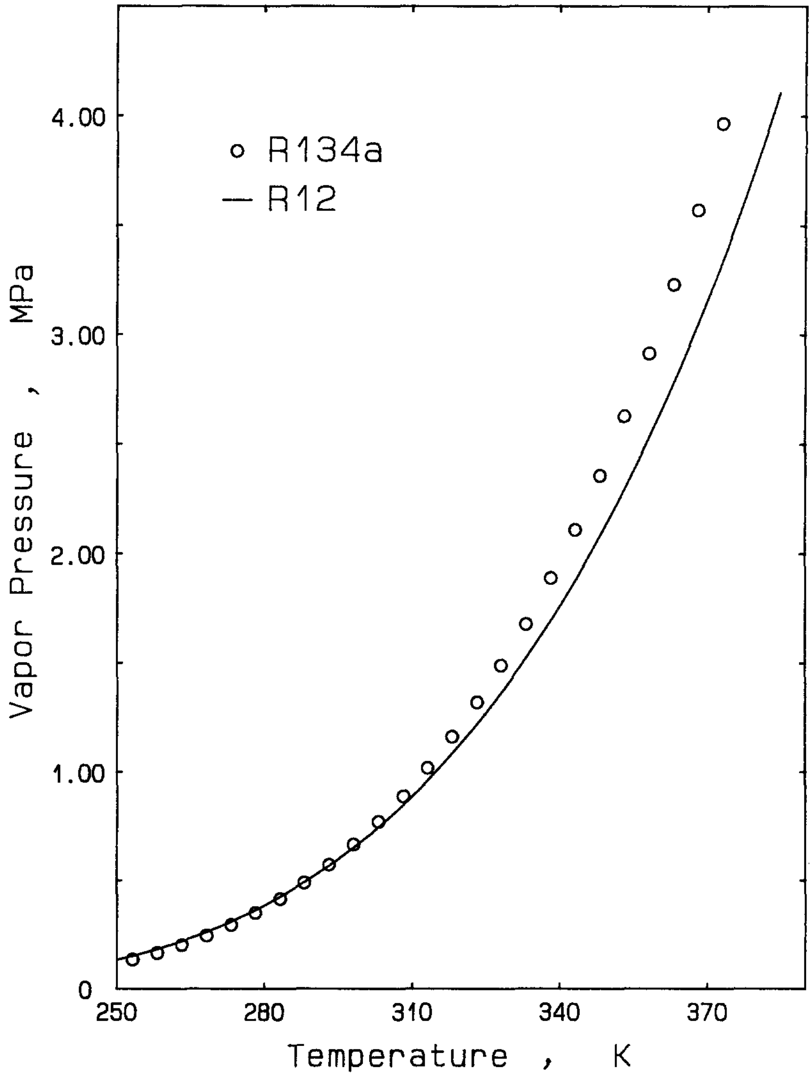

Fig. 3. Vapor pressures of R134a and R12.

3. RESULTS AND DISCUSSION

The measured vapor pressures are plotted against temperature and are shown in Figs. 2 to 4, with the data for R11, R12, and R113, respectively. The vapor pressures of R123 and R123a are very similar to those of R11 over the whole experimental temperature range, but the vapor pressures of R134a show some differences from those of R12 as the temperature

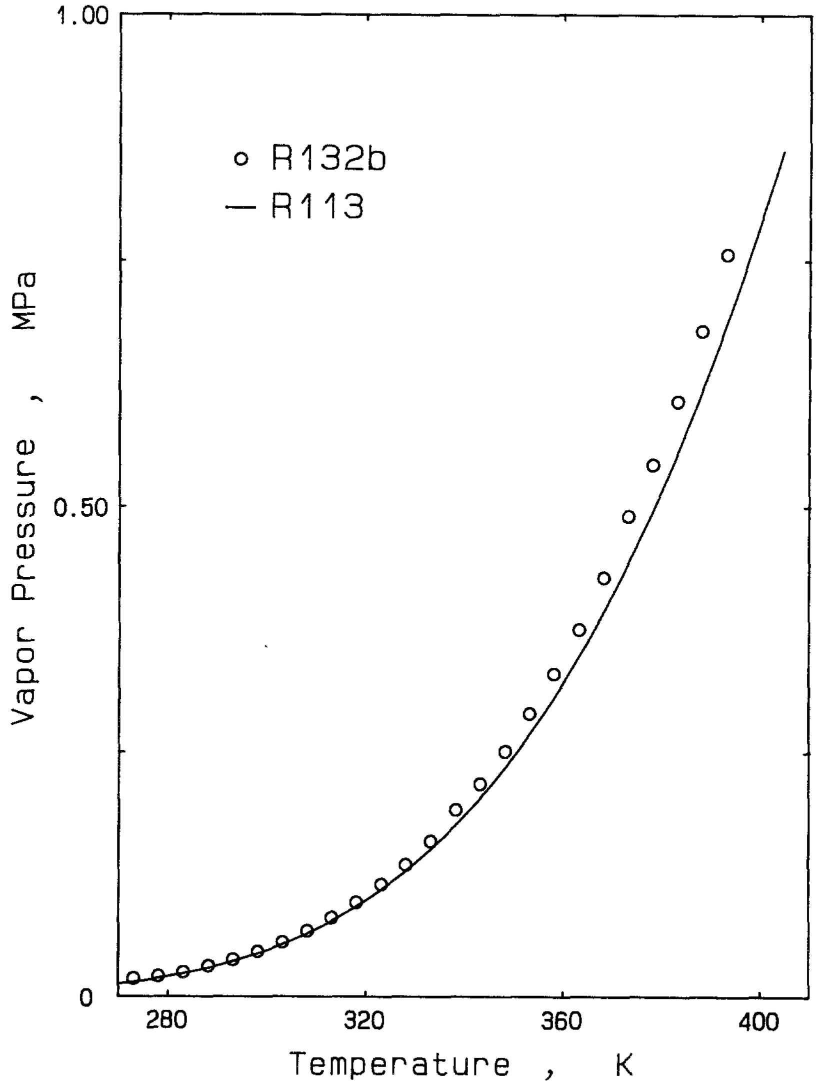

Fig. 4. Vapor pressures of R132b and R113.

Table I. Experimental and Calculated Vapor Pressure

	P (kPa)							
	R123		R123a		R134a		R132b	
T (K)	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
253.15					133.2	133.2		
258.15					164.6	164.7		
263.15					201.7	201.5		
268.15					244.2	244.2		
273.15	34.4	34.3			293.6	293.6	14.2	14.2
278.15	42.3	42.4			349.9	350.3	18.5	18.4
283.15	51.8	52.1			414.7	415.0	23.5	23.5
288.15	63.7	63.5			489.0	488.6	29.6	29.6
293.15	77.5	76.9			571.6	571.9	36.8	36.9
298.15	92.8	92.5			665.6	665.5	45.3	45.6
303.15	110.3	110.5	102.0	102.4	769.9	770.3	56.0	55.7
308.15	131.8	131.3	122.7	122.2	888.3	887.2	67.7	67.5
313.15	155.0	155.1	145.5	144.7	1017.8	1016.9	81.6	81.3
318.15	181.7	182.2	169.7	170.1	1160.1	1160.2	97.2	97.1
323.15	212.0	212.9	198.6	198.6	1318.3	1317.9	115.6	115.4
328.15	246.3	247.4	230.8	230.8	1489.1	1490.9	135.6	136.2
333.15	285.1	286.1	265.7	266.8	1677.5	1680.1	159.6	159.9
338.15	328.3	329.2	306.0	307.0	1888.7	1886.5	185.7	186.6
343.15	379.5	377.2	352.2	351.8	2109.5	2111.3	216.6	216.8
348.15	431.1	430.2	402.0	401.5	2356.1	2356.0	251.2	250.6
353.15	488.6	488.7	457.6	456.7	2626.8	2622.3	289.4	288.2
358.15	552.9	552.9	519.0	517.5	2913.8	2912.8	329.9	329.9
363.15	624.2	623.3	582.2	584.5	3230.3	3230.2	374.9	376.0
368.15	700.8	700.1	657.0	657.9	3571.5	3578.7	427.8	426.6
373.15	785.6	783.7	739.4	738.1	3967.2	3963.3	482.0	482.0
378.15	874.8	874.6	828.2	825.5			543.2	542.5
383.15	973.1	973.1	919.2	920.3			607.7	608.4
388.15	1084.5	1079.7	1022.4	1022.8			679.1	680.0
393.15	1196.7	1194.9	1136.8	1133.2			757.0	757.8
398.15	1315.9	1319.1	1248.5	1251.9			843.5	842.3
403.15	1442.3	1453.0	1377.3	1379.1				
408.15	1596.8	1597.1	1511.5	1515.1				
413.15	1752.2	1752.2	1660.5	1660.3				
418.15	1913.3	1918.9	1818.3	1815.3				
422.17	2066.2	2061.9						
423.25			1983.5	1984.1				
427.78	2270.6	2275.8						
428.25			2160.5	2161.0				
432.78	2475.5	2481.5						
433.05			2341.7	2342.6				
437.57			2533.9	2525.6				
437.87	2727.4	2706.8						
442.65	2944.0	2933.9						
443.26			2774.3	2774.7				
447.47	3178.3	3179.5						
448.32			3006.6	3017.0				
453.15			3276.5	3270.2				
453.75	3511.5	3526.6						
457.38	3745.3	3742.5						
458.26			3565.1	3566.1				

Table II. Coefficients of the Vapor Pressure Equation (1)

	R123	R123a	R134a	R132b
A_0	−316.44	−108.41	6.1609	−1202.3
A_1	758.26	632.60	509.43	544.10
A_2	−2.0396	−1.1688	−1.7204	−13.0786
A_3	4.1983	2.7628	2.2016	2.3054
A_4	1.5918	1.3226	0.44718	−1.1159
A_5	−0.17239	−1.3539	0.41553	0.62946
Mean dev. (%)	0.28	0.20	0.07	0.24
Max dev. (%)	0.80	0.56	0.20	0.55

increases. Although R132b is not regarded as an alternative to R113 at present, due to its weak toxicity, its vapor pressures are plotted in Fig. 4 with those of R113. The numerical vapor pressure data are presented in Table I.

Several vapor pressure equations were examined to fit the present experimental vapor pressures, and among them, the best formula was selected for this correlation under the condition where the precise critical values are not available. The vapor pressures obtained are fitted by the following equation [1]:

$$T \ln P = A_0/2 + \sum_{i=1}^{5} A_i E_i(x) \tag{1}$$

where P is the vapor pressure in kPa, T is the temperature in K, and $A_0 \sim A_5$ are constant. The variable x is defined by the following equation, using the applicable range between T_{max} and T_{min}:

$$x = \{2T - (T_{max} + T_{min})\}/(T_{max} - T_{min})$$

$E_i(x)$ is the Chebyshev polynomial, where $E_0(x) = 1$, $E_1(x) = x$, and $E_{i+1}(x) - 2xE_i(x) + E_{i-1}(x) = 0$.

Table III. Normal Boiling Points of R123, R123a, R134a, and R132b in K

	R123	R123a	R134a	R132b
This work	300.7	302.7	246.9	319.7
Allied-Signal Inc. (1987)	301.0		246.99	
ICI Chemicals & Polymers, Ltd. (1988)	300.3		247.0	
E. I. du Pont (1988)	301		246.7	

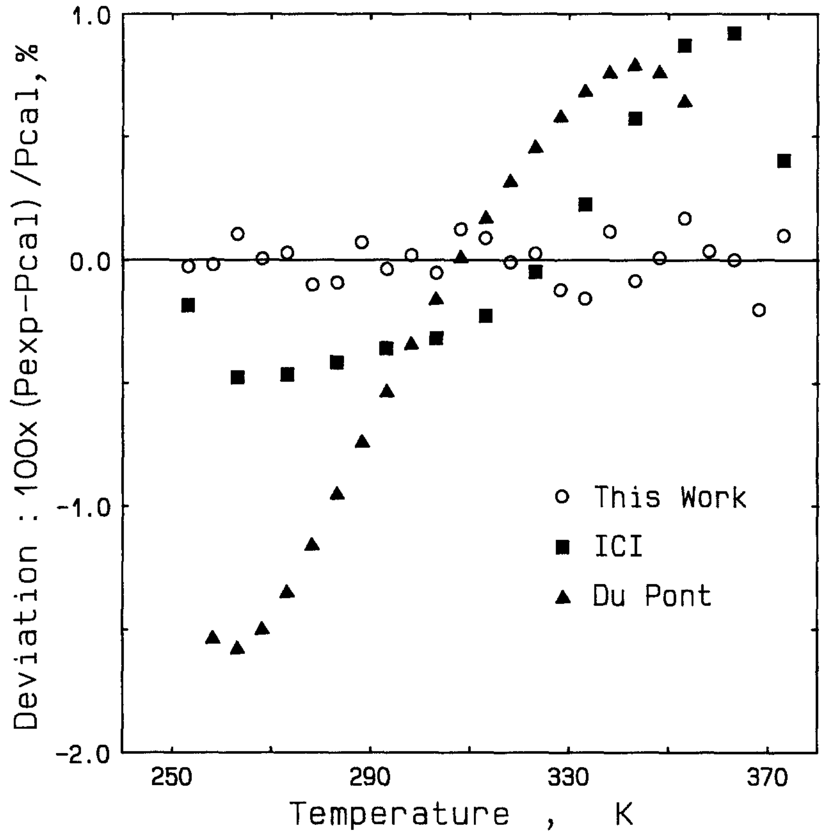

Fig. 5. Relative deviations of vapor pressure of R134a from values calculated by Eq. (1).

The numerical constants of Eq. (1) were determined by a least-squares technique and are listed in Table II together with average and maximum deviations. The calculated vapor pressures from Eq. (1) are also listed in Table I.

The normal boiling points of these compounds except R134a are calculated from Eq. (1), whereas that of R134a, whose value is out of the

Table IV. Critical Temperature and Pressure of R134a

	This work	ICI [2]	Kabata et al. [5]	Basu et al. [6]
Critical temperature (K)	374.27	379.65	374.30 ± 0.01	374.25 ± 0.15
Critical pressure (kPa)	4065	3648		4067 ± 5

experimental temperature range, is estimated by the extrapolation using the Antoine equation. The obtained values are listed in Table III with some values from the manufacturers' data sheets.

A deviation plot of experimental vapor pressure of R134a from Eq. (1) is shown in Fig. 5. Two preliminary reports on the vapor pressure of R134a are available. The values of ICI [2] agree with ours within 0.5% excluding a few data points. The values of du Pont [3] deviate from −1.6% to +0.8% from our values.

The critical temperature of R134a has been determined preliminarily by visual observation of the disappearance of the meniscus at the vapor–liquid interface. The critical pressure is calculated from the Ambrose equation [4] using this preliminary critical temperature. These values are listed in Table IV in addition to literature values [2, 5, 6].

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