Vapor Pressures of Fluorobenzenes from 5° to 50° C.

T. J. V. FINDLAY[1]
School of Chemistry, The University of Bristol, Bristol, U. K.

A static apparatus was used to measure the vapor pressures of 1,3,5-trifluoro- and 1,2,3,4-tetrafluorobenzene over the range 5° to 50° C. Data are also included for hexafluorobenzene, for comparison with the literature, and for a relatively impure sample of 1,2,3,5-tetrafluorobenzene. The enthalpies of evaporation have been estimated.

INCREASING interest is being taken in the thermodynamic properties of the fluorobenzenes either on their own (*1, 5, 10, 17, 20*) or in mixtures with hydrocarbons (*11, 13, 14*). In recent years most of the homologs have become available, but the vapor pressures of some of these have not yet been measured. The purpose of the present work was to measure the vapor pressures of 1,3,5-trifluoro-, 1,2,3,4,-tetrafluoro-, and 1,2,3,5-tetrafluorobenzenes, to make possible the calculation of activity coefficients from GLC work (*7, 13*). For comparison with earlier work, data were also obtained for hexafluorobenzene.

EXPERIMENTAL

Purification. The samples used were identical to those used by Gainey (*13*) and had been supplied by Imperial Smelting Corp., Ltd., Avonmouth, U. K. They were not further purified, but the purity was checked by GLC. The approximate mole percentages given in Table I are based on peak heights. From a comparison of retention times of the impurities and an assumption that Raoult's law is obeyed, the effect on the vapor pressure was estimated. Only the first two, and possibly the third, are satisfactory. Nevertheless, vapor pressure data are included for 1,2,3,5-tetrafluorobenzene, since the sample used seems to be the best available at present.

Vapor Pressure Measurement. The apparatus was a conventional McBain balance (*4*) from which the spiral spring had been removed. The cell consisted of the empty balance tube surrounded by a silvered water jacket. Water was pumped to the jacket from a thermostat, equipped with external electric lamps as heaters and a Rheinische TKI refrigerator. The temperature was controlled by a mercury-toluene regulator and was constant to better than ±0.01° C. in the water jacket. The thermometers used had recently been calibrated by the National Physical Laboratory, Teddington, U. K.

The pressure was measured on a mercury U-tube manometer, constructed from 19.5-mm. diameter tubing, by means of a Precision Tool and Instrument Co. cathetometer fitted with a vernier scale reading to 0.01 mm. An air thermostat, surrounding the manometer and the jacketed cell, was held constant to ±0.04° C. at a temperature at least 1° C. above the temperature in the cell.

The liquid was repeatedly degassed in a conventional vacuum line and distilled through mercury cutoffs to the cell. Vapor pressure readings were made at a series of temperatures, allowing at least 2 hours for equilibrium to be reached. The readings were corrected to torr (760 torr = 1 standard atmosphere) and were estimated to be uncertain to ±0.05 torr.

RESULTS

The vapor pressure results are presented in Table II. They have been fitted to the Antoine equation,

$$\log_{10}P(\text{torr}) = A - B/(t\,°\,\text{C.} + C)$$

by a linear least squares fit in three dimensions to the transformed equation (*16, 21*)

$$C \log P + t \log P = (AC - B) + At$$

In the case of hexafluorobenzene, the result at 4.74° C.

Table I. Purity of Fluorobenzenes

		Impurities			
		More Volatile		Less Volatile	
Fluorine Positions	Purity, Mole %	Mole %	Effect on *P*, %	Mole %	Effect on *P*, %
Hexa-	99.91	0.02	+0.004	0.07	−0.02
1,3,5-	99.99				
1,2,3,4-	99.0	0.39	+0.17	0.60	−0.20
1,2,3,5-	94.9	0.02	+0.01	5.1	−1.0

Table II. Vapor Pressures of Fluorobenzenes

Hexa-		1,3,5-		1,2,3,4-		1,2,3,5-	
Temp., ° C.	*P*, torr	Temp., ° C.	*P*, torr	Temp., ° C.	*P*, torr	Temp., ° C.	*P*, torr
4.74	28.87	6.18	40.39	6.05	17.89	6.08	27.54
5.70	30.49	6.19	40.42	6.06	17.83	6.12	27.49
7.07	33.20	10.03	49.62	10.36	22.81	10.29	34.64
7.14	33.22	15.01	63.98	15.21	29.73	10.29	34.69
9.77	38.39	15.01	64.01	15.21	29.78	15.21	45.12
17.23	57.35	19.99	81.87	20.64	39.58	15.24	45.20
17.23	57.38	19.99	81.84	20.64	39.61	19.77	57.08
19.88	65.68	20.49	84.02	24.82	49.09	19.77	57.04
24.28	81.87	20.53	84.08	24.82	49.11	24.81	73.23
24.40	82.42	22.79	93.52	29.98	63.25	24.81	73.28
25.10	85.52	25.21	104.77	29.99	63.25	29.78	92.78
27.08	93.84	25.24	104.90	35.05	80.42	29.78	92.85
29.92	107.23	29.98	129.99	35.06	80.42	35.01	117.98
29.92	107.26	29.98	130.05	40.07	100.79	35.03	118.07
29.92	107.28	35.15	162.61	40.07	100.80	39.89	146.04
35.92	141.18	35.25	163.56	43.99	119.29	39.89	146.08
41.81	182.18	35.29	163.86	44.01	119.40	44.81	179.45
47.32	228.44	40.05	199.92	46.91	135.19	44.81	179.51
47.85	233.00	40.11	200.30	46.91	135.19	49.83	220.24
		43.85	232.66	48.82	147.16	49.83	220.31
		43.94	233.93	48.83	147.17		
		44.20	235.99	49.84	152.86		
		46.97	263.69	49.87	153.22		
		46.97	263.78				
		49.98	295.92				
		49.99	295.99				
		49.99	295.99				

---

[1] Present address: School of Chemistry, The University of New South Wales, Kensington, N.S.W. 2033, Australia.

was not used in the computation, since it was below the triple point of 5.17° C. (*9*). The standard deviations in the last column of Table III are consistent with the experimental uncertainty in t and P.

DISCUSSION

In the case of hexafluorobenzene, there are a number of published results. These are compared with the present data in Figure 1, where ΔP = (published pressure) − (pressure calculated from the Antoine constants in Table III). The dashed curves indicate extrapolation beyond the temperature ranges in which measurements were made. The results of Evans and Tiley (*10*) measured from 96° to 242° C. on a static apparatus have not been included, since $\Delta P = 10.4$ torr at 20° C. There seems to be reasonable agreement between the results illustrated, bearing in mind the extrapolations involved. An attempt was made to fit a combination of the present results with those of Counsell (*5*) and Douslin (*9*), but the large standard deviation of 0.30 torr with $A = 7.06067$, $B = 1244.000$, $C = 217.352$ indicated that such combination may not be justified.

The enthalpy of evaporation was calculated from the equation (*6*),

$$\Delta H_e = \frac{2.3026\, BT}{(t + C)^2}\,[RT + (B^* - v)\, P]$$

where B and C are the constants in the Antoine equation, B^* is the second virial coefficient of the vapor, and v is the molar volume of the liquid. Values of B^* at each temperature were obtained by interpolation between the values for monofluorobenzene (*19*), 1,2-difluorobenzene (*20*), and hexafluorobenzene (*5*), assuming that the variation of B^* with the number and positions of substituted fluorines follows a pattern similar to the variation of boiling points (Table V). Values of v were estimated from known densities (*5, 12, 15*), assuming that the coefficient of cubical expansion of hexfluorobenzene, 1.41×10^{-3} (*5*), was the same for all fluorobenzenes. Since the B^* and v values are used only for making gas phase imperfection corrections, use of these estimates is justifiable. The ΔH_e values so calculated are given in Table IV. The values in parentheses were calculated at temperatures outside the range of vapor pressure measurements and cannot therefore be considered seriously. Nevertheless, the reasonable agreement between the various estimates for hexafluorobenzene suggests that the present estimates for the other fluorobenzenes are the best that can be obtained until precise values of the second virial coefficients of the vapors are available.

Table III. Constants in the Antoine Equation

Fluorine Positions	A	B	C	σ, Torr
Hexa-	6.86088	1152.442	208.663	0.17
1,3,5-	6.91873	1196.385	219.019	0.14
1,2,3,4-	7.19386	1396.067	228.873	0.16
1,2,3,5- (95%)	7.07758	1290.984	222.855	0.11

Table IV. Calculated Enthalpies of Evaporation

(Kilojoules per mole)

Fluorine Positions	Temp., ° C.				
	10	25	40	70	100
Hexa-					
This work	36.72	35.47	34.29	(32.00)	(29.61)
(*5*)	(36.74)	(35.69)	34.62	32.42	(30.14)
(*9*)	36.80	35.68	34.62	32.50	30.20
(*17*)	(35.64)	34.95	34.24	32.69	(30.81)
(*10*)				(31.53)	29.72
1,3,5-	34.73	33.74	32.79		
1,2,3,4-	37.40	36.61	35.86		
1,2,3,5- (95%)	36.3	35.4	34.5		

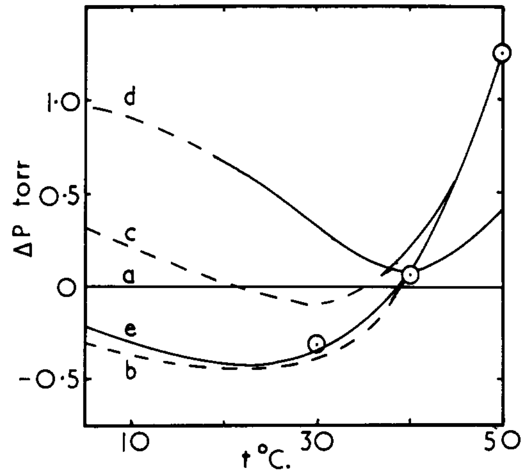

Figure 1. Comparison of vapor pressures of hexafluorobenzene

ΔP = (published pressure) − [pressure calculated from log P = 6.86088 − 1152.442/(t° C. + 208.663)]

a. Present work, 6° to 48° C., static apparatus
b. Counsell *et al.* (*5*), 37° to 89° C., dynamic apparatus, Antoine equation
c. As *b* but using Kirchhoff equation
d. Patrick and Prosser (*17*) 20° to 85°C., static apparatus
e. Douslin and Osborn (*9*), 5° C., static apparatus; 20° to 114° C., dynamic apparatus
⊙ Gaw and Swinton (*14*) 30° to 70° C., static apparatus

The enthalpies of evaporation for the fluorobenzene series follow the same pattern as the boiling points (Table V).

ACKNOWLEDGMENT

The author is grateful to D. H. Everett and A. J. B. Cruickshank for providing research facilities at the University of Bristol; and to the Royal Society and Nuffield Foundation Commonwealth Bursaries Scheme and The Uni-

Table V. Boiling Points and Enthalpies of Evaporation of Fluorobenzenes

Fluorine Positions	B.P., ° C.	ΔH_e, Kj/ Mole at 25° C.	Fluorine Positions	B.P., ° C.	ΔH_e, Kj/ Mole at 25° C.
0-	80.1	33.84 (*3*)	1,3,5-	77.3	33.74
1-	84.7 (*19*)	34.53 (*19*)	1,2,3,4-	94.8	36.61
1,2-	93.9 (*20*)	36.17 (*20*)	1,2,3,5- (95%)	84.8	35.4
1,3-	83.0 (*8*)	34.55 (*8*)	1,2,4,5-	90.3 (*2*)	37.11 (*2*)
1,4-	88.9 (*8*)	35.68 (*8*)	Penta-	84.7 (*17*)	36.39 (*1*)
1,2,4-	88 (*18*)		Hexa-	80.3 (*5*)	35.47

versity of New South Wales for providing financial assistance. Grateful acknowledgment is also made to C. Hicks and T. Letcher for help with the computations. The fluorobenzenes were kindly donated by the Imperial Smelting Corp., Ltd., Avonmouth.

LITERATURE CITED

(1) Ambrose, D., *J. Chem. Soc. Inorg. Phys. Theor.* **1968**, 1381.
(2) Ambrose, D., calculated from unpublished data supplied by D. Ambrose, National Physical Laboratory, Teddington, U. K.
(3) Andon, R.J.L., Cox, J.D., Herington, E.F.G., Martin, J.F., *Trans. Faraday Soc.* **53**, 1074 (1957).
(4) Ashworth, A.J., Everett, D.H., *Ibid.*, **56**, 1609 (1960).
(5) Counsell, J.F., Green, J.H.S., Hales, J.L., Martin, J.F., *Ibid.*, **61**, 212 (1965).
(6) Cruickshank, A.J.B., Cutler, A.J.B., J. CHEM. ENG. DATA **12**, 326 (1967).
(7) Cruickshank, A.J.B., Windsor, M.L., Young, C.L., *Proc. Roy. Soc. (London) Ser. A* **295**, 259 and 271 (1966).
(8) Douslin, D.R., calculated from unpublished data supplied by A. Osborn and D.R. Douslin, Bureau of Mines, Bartlesville, Okla.
(9) Douslin, D.R., Osborn, A., *J. Sci. Instr.* **42**, 369 (1965).
(10) Evans, F.D., Tiley, P.F., *J. Chem. Soc. Phys. Org.* **1966**, 134.
(11) Fenby, D.V., McLure, I.A., Scott, R.L., *J. Phys. Chem.* **70**, 602 (1966).
(12) Finger, G.C., Reed, F.H., Finnerty, J.L., *J. Am. Chem. Soc.* **73**, 153 (1951).
(13) Gainey, B.W., Ph.D. thesis, University of Bristol, U.K., 1967.
(14) Gaw, W.J., Swinton, F.L., *Trans. Faraday Soc.* **64**, 637 (1968).
(15) Imperial Smelting Corp., Ltd., Avonmouth, private communication to A.J.B. Cruickshank, University of Bristol, 1967.
(16) Lark, P.D., Craven, B.R., Bosworth, R.C.L., "Handling of Chemical Data," p. 249, Pergamon Press, London, 1968.
(17) Patrick, C.R., Prosser, G.S., *Trans. Faraday Soc.* **60**, 700 (1964).
(18) Schiemann, G.J., *J. prakt. Chem.* **140**, 97 (1934).
(19) Scott, D.W., McCullough, J.P., Good, W.D., Messerly, J.F., Pennington, R.E., Kincheloe, T.C., Hossenlopp, I.A., Douslin, D.R., Waddington, G., *J. Am. Chem. Soc.* **78**, 5457 (1956).
(20) Scott, D.W., Messerly, J.F., Todd, S.S., Hossenlopp, I.A., Osborn, A., McCullough, J.P., *J. Chem. Phys.* **38**, 532 (1963).
(21) Willingham, C.B., Taylor, W.J., Pignocco, J.M., Rossini, F.D., *J. Res. Natl. Bur. Stand.* **35**, 219 (1945).

RECEIVED for review May 31, 1968. Accepted December 9, 1968.

Enthalpies of Combustion and Formation of 11 Isomeric Nonanes

WILLIAM D. GOOD
Bartlesville Petroleum Research Center, Bureau of Mines, U. S.
Department of the Interior, Bartlesville, Okla. 74003

The enthalpies of combustion of 11 isomeric nonanes were determined by oxygen-bomb combustion calorimetry. Enthalpies of combustion were computed from measurements of mass of samples burned and mass of carbon dioxide produced. The following values, in kilocalories per mole based on the mass of sample, are reported for the standard enthalpy of combustion, $\Delta Hc^\circ_{298.15}$, of these compounds in the liquid state: *n*-nonane, −1463.96 ± 0.13; 2,2-dimethylheptane, −1460.74 ± 0.20; 2,2,3-trimethylhexane, −1462.05 ± 0.18; 2,2,4-trimethylhexane, −1462.01 ± 0.20; 2,2,5-trimethylhexane, −1459.50 ± 0.20; 2,3,3-trimethylhexane, −1462.43 ± 0.20; 2,3,5-trimethylhexane, −1461.73 ± 0.20; 2,4,4-trimethylhexane, −1462.65 ± 0.18; 3,3,4-trimethylhexane, −1463.28 ± 0.18; 2,2-dimethyl-3-ethylpentane, −1464.44 ± 0.18; and 2,4-dimethyl-3-ethylpentane, −1465.15 ± 0.18. The experimental results for these compounds were compared to values predicted by current correlative procedures.

THE BUREAU OF MINES is conducting thermodynamic studies on selected hydrocarbons under American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum." One of the experimental goals of this program is the provision of basic thermodynamic data on a limited number of carefully selected compounds. From these basic data the thermodynamic properties for many other compounds can be calculated by correlation. As part of this continuing program, the enthalpies of combustion of 11 isomeric nonanes were determined and are reported. Johnson *et al.* (*12*) have contributed experimental enthalpies of combustion of five other highly branched nonanes. The present research adds 10 experimental values for branched-chain nonanes in addition to a new value for *n*-nonane, so experimental values now are available for 16 of the 35 nonanes.

The API Research Project 44 tables (*2*) contain experimental enthalpy-of-formation data for the alkanes of molecular weight as high as the octanes with a few exceptions. Data for two of the heptanes, 2-methylhexane and 3-methylhexane, are correlated values. New experimental evidence (*14*) also indicates that the older experimental enthalpy-of-formation data for the pentanes, particularly neopentane, need adjustment in the tables.

Many attempts have been made to correlate the enthalpy-of-formation data of the alkanes with their molecular structure. Some of these correlations have been more successful than others, and perhaps the most successful of the recent correlative procedures have been the Allen (*1*) method, the modification of the Allen method by Skinner (*20*), the Rossini-Greenshields (*9*) method, and the Somayajulu-Zwolinski (*21*) method. All of these correlative