Vapor Pressures and Boiling Points of the 1-Fluoroalkanes, 1-Chloroalkanes, 1-Bromoalkanes, and 1-Iodoalkanes, C_1 to C_{20}

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AS PART of its systematic program on the collection, analysis, calculation, correlation, and compilation of data on the physical and thermodynamic properties of the chemical substances, the Manufacturing Chemists' Association Research Project has investigated the data on vapor pressures for a large number of substances. This report presents the results for the first 20 members, C_1 to C_{20}, of the series of 1-fluoroalkanes, 1-chloroalkanes, 1-bromoalkanes, and 1-iodoalkanes.

EXISTING DATA

The existing data on these compounds over a range of pressures are relatively meager. Complete data on vapor pressures are available only for the first several members of each of the four series of compounds. For the higher members of each series, the data are limited to low pressures.

Table I summarizes the number of pairs of P-T values available as experimental measurements for these compounds, excluding the data at pressures near 760 mm. of mercury.

Table I. Summary of Pairs of Experimental P-T Values in the Literature for the Four Series of Compounds, C_1 to C_{20}, Excluding Data at Pressures Near 760 Mm. of Mercury

No. of Carbon Atoms	Number of Pairs of Experimental P-T Values in the Literature			
	1-Fluoro-alkanes	1-Chloro-alkanes	1-Bromo-alkanes	1-Iodo-alkanes
1	60	40	27	21
2	6	47	56	19
3	10	15	4	14
4	0	22	1	5
5	0	5	1	5
6	0	2	4	4
7	0	3	4	5
8	0	4	8	4
9	0	2	10	1
10	0	6	11	4
11	1	2	6	2
12	0	7	12	2
13	0	0	1	1
14	0	3	5	2
15	0	4	1	1
16	2	3	4	8
17	0	1	1	1
18	0	3	4	2
19	0	0	1	1
20	0	1	0	1

The existing data on the boiling points at pressures near 760 mm. of mercury are relatively more abundant. A complete set of references to the literature for data on these compounds is given in tables (5) and not repeated here. The data available for these compounds on boiling points at pressure near 760 mm. of mercury are: 1-fluoroalkanes, C_1 to C_8, C_{10}, C_{16}; 1-chloroalkanes, C_1 to C_{12}; 1-bromoalkanes, C_1 to C_9; 1-iodoalkanes, C_1 to C_8. No data at pressures near 760 mm. of mercury were available for 10 of the 1-fluoroalkanes, eight of the 1-chloroalkanes, 10 of the 1-bromoalkanes, and 12 of the 1-iodoalkanes.

CORRELATION OF THE DATA

For each compound having data available, all the information at pressures near 760 mm. of mercury was critically examined and a "best" value selected. Then for the members of each series, these selected values for the normal boiling points were compared with the method of correlation developed in this laboratory (2). This method relates the normal boiling points with the number of carbon atoms in the normal alkyl chain by the following equation:

$$t = t_0 + c_i' \log(m-1) - d_i \left\{ \int_{b_i}^{\infty} e^{-u}\, d\ln u - \int_{u}^{\infty} e^{-u}\, d\ln u \right\} \quad (1)$$

Equation 1 applies to any normal alkyl series of compounds, as represented by the general formula, Y-$(CH_2)_m$-H. In Equation 1, t is the normal boiling point at 760 mm. of mercury, m is the number of carbon atoms in the normal alkyl radical, $u = b_i(m-1)$, b_i is taken equal to 0.1505 for all normal alkyl series, and the constants t_0, c_i', and d_i are characteristic of each given normal alkyl series. The values of the definite integrals in Equation 1, for values of m from 2 to 40, are given in Table IV of (2).

Because of the paucity of data on the compounds of the present investigation, the value of c_i' was taken as 540 for each of the four series, the selection being based on the values of c_i' reported for eight other normal alkyl series, together with the available data on the compounds of the present report. With the values of c_i' thus fixed for a given series, the available data are used to obtain values for the constants t_0 and d_i. With the constants so evaluated, the values of the normal boiling points were calculated for the 40 compounds for which no experimental data were available at pressures near 760 mm. of mercury.

For the present investigation, the Antoine equation,

$$\log P = A - B/(C + t) \quad (2)$$

was used because earlier work in this laboratory had demonstrated its effectiveness (3, 4). For those cases where

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sufficient data are not available to evaluate all the constants, several methods may be used to estimate values of the constant C.

Thomson (6) gives the equation

$$C = 239 - 0.19t_B \quad (3)$$

where t_B is the normal boiling point. This relation—excellent for compounds having a small number of carbon atoms, five or less—gives values within several units for compounds with about 10 carbon atoms, and values within about 20 units for compounds in the range 15 to 20 carbon atoms. Since the Antoine equation is mathematically relatively insensitive to the value of C, being self-adjusting in the values of A and B, a value of C good to within 20 units can reproduce data on vapor pressures reasonably well. Table II gives a comparison of the values of constant C calculated from Equation 3 with the values obtained from the adequate experimental data available for 11 compounds. As may be seen, the accord is excellent for these compounds.

Table II. Comparison of Values of Constant C Calculated with Equation 3 with Values Obtained from Adequate Experimental Data Available for 11 Compounds

Compound	Values of Constant C: Derived from experimental data	Values of Constant C: Calculated from Equation 3
CH_3F	252	254
C_2H_5F	240	246
n-C_3H_7F	241	240
CH_3Cl	245	244
C_2H_5Cl	237	237
n-C_4H_9Cl	219	224
CH_3Br	244	238
C_2H_5Br	232	233
n-C_3H_7Br	230	226
CH_3I	232	231
C_2H_5I	227	225

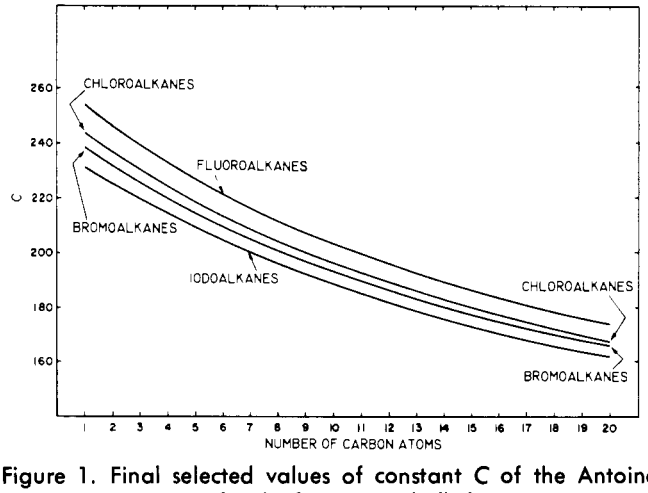

Figure 1. Final selected values of constant C of the Antoine equation for the four normal alkyl series

Another method for evaluating constant C is given by Dreisbach (1) in the form of an equation applicable for each given Cox chart family. For those cases where the data are meager, however, Equation 3 serves adequately, and is used here because the proper use of the Dreisbach procedure (1) requires more experimental data than were available. Figure 1 gives a plot of the values of C as a function of the number of carbon atoms in the normal alkyl radical, for each of the four series of compounds.

With the value of C thus determined, the value of the selected normal boiling point, and the data on the lower vapor pressures well removed from 760 mm. of mercury were used to obtain preliminary values of the constants A and B, for those compounds for which data were available. These values of B were plotted as a function of the number of carbon atoms in the normal alkyl radical, for each series. The curves were smoothed by taking first and second differences in the values between successive members of a series. The final value of B was taken from the smoothed curves (Figure 2).

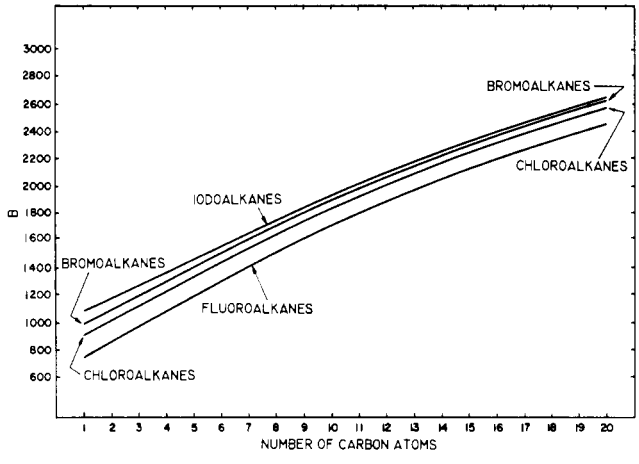

Figure 2. Final selected values of constant B of the Antoine equation for the four normal alkyl series

With the final values of B and C so obtained, the final values of A were calculated from the selected values of the normal boiling point. Figure 3 gives a plot of the values of A as a function of the number of carbon atoms, for each of the four series of compounds.

RESULTS

Table III gives the values of A, B, and C for the Antoine equation, applicable within certain limits, for pressures in the range of 10 to 1500 mm. of mercury for all 80 compounds.

The following tables (5) give a numerical value of the temperature for 27 selected values of pressure in the range 10 to 1500 mm. of mercury:

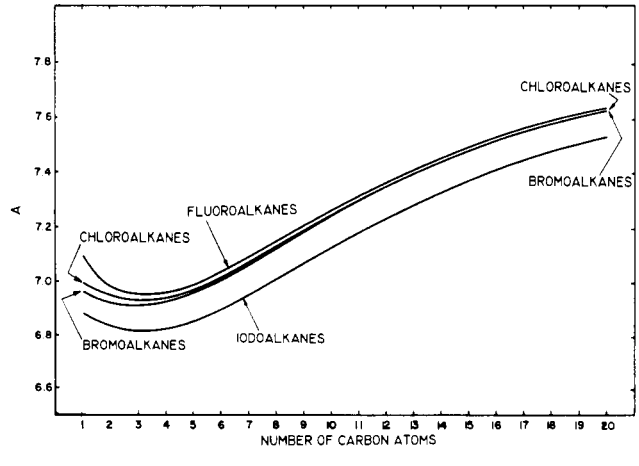

Figure 3. Final selected values of constant A of the Antoine equation for the four normal alkyl series

Table III. Values of the Constants of the Antoine Equation for Vapor Pressures, Applicable within Certain Limits, for Pressures in the Range of 10 to 1500 Mm. of Hg for C_1 to C_{20} Compounds

$LOg_{10}P = A - B/(C + t)$; $t[B/(A - \log_{10} P)] - C$; P = mm. Hg and t = ° C.

Compound	Values of Constants		
	A	*B*	*C*
1-Fluoroalkanes			
1-Fluoromethane (methyl fluoride)	7.09761	740.218	253.89
1-Fluoroethane (ethyl fluoride)	6.97853	854.211	246.16
1-Fluoropropane	6.9533	965.18	239.5
1-Fluorobutane	6.9581	1081.71	232.8
1-Fluoropentane	6.9857	1190.03	227.1
1-Fluorohexane	7.0305	1299.19	221.6
1-Fluoroheptane	7.0835	1405.79	216.6
1-Fluoro-octane	7.1411	1509.34	212.0
1-Fluorononane	7.1977	1608.48	207.6
1-Fluorodecane	7.2542	1704.75	203.6
1-Fluoroundecane	7.308	1797.8	200
1-Fluorododecane	7.357	1885.6	196
1-Fluorotridecane	7.406	1969.1	193
1-Fluorotetradecane	7.449	2048.3	190
1-Fluoropentadecane	7.488	2123.4	187
1-Fluorohexadecane	7.520	2194.8	184
1-Fluoroheptadecane	7.556	2262.5	181
1-Fluoro-octadecane	7.586	2327.4	179
1-Fluorononadecane	7.612	2389.7	176
1-Fluoroeicosane	7.636	2450.1	174
1-Chloroalkanes			
1-Chloromethane (methyl chloride)	6.99445	902.451	243.60
1-Chloroethane (ethyl chloride)	6.94914	1012.771	236.67
1-Chloropropane	6.93111	1121.123	230.20
1-Chlorobutane	6.93790	1227.433	224.10
1-Chloropentane	6.96617	1332.890	218.50
1-Chlorohexane	7.0115	1437.05	213.4
1-Chloroheptane	7.0650	1539.35	208.8
1-Chloro-octane	7.1231	1639.20	204.4
1-Chlorononane	7.1802	1736.11	200.4
1-Chlorodecane	7.2372	1829.68	196.6
1-Chloroundecane	7.2917	1919.62	193.0
1-Chlorododecane	7.3394	2005.72	190.0
1-Chlorotridecane	7.391	2087.9	186
1-Chlorotetradecane	7.434	2166.1	184
1-Chloropentadecane	7.474	2240.5	180
1-Chlorohexadecane	7.506	2311.4	178
1-Chloroheptadecane	7.543	2378.8	175
1-Chloro-octadecane	7.573	2443.5	173
1-Chlorononadecane	7.600	2505.7	170
1-Chloroeicosane	7.624	2566.1	168

Compound	Values of Constants		
	A	*B*	*C*
1-Bromoalkanes			
1-Bromomethane (methyl bromide)	6.95965	986.590	238.32
1-Bromoethane (ethyl bromide)	6.91995	1090.810	231.71
1-Bromopropane	6.91065	1194.889	225.51
1-Bromobutane	6.92254	1298.608	219.70
1-Bromopentane	6.95580	1401.634	214.38
1-Bromohexane	7.0023	1503.52	209.5
1-Bromoheptane	7.0582	1603.71	205.0
1-Bromo-octane	7.1179	1701.61	200.8
1-Bromononane	7.1761	1796.73	196.9
1-Bromodecane	7.2336	1888.67	193.3
1-Bromoundecane	7.2882	1977.14	189.8
1-Bromododecane	7.3390	2061.93	186.6
1-Bromotridecane	7.386	2143.0	184
1-Bromotetradecane	7.430	2220.2	181
1-Bromopentadecane	7.470	2293.8	178
1-Bromohexadecane	7.506	2364.0	175
1-Bromoheptadecane	7.540	2430.9	173
1-Bromo-octadecane	7.570	2495.2	170
1-Bromononadecane	7.597	2557.2	168
1-Bromoeicosane	7.621	2617.5	166
1-Iodoalkanes			
1-Iodomethane (methyl iodide)	6.87991	1093.235	230.94
1-Iodoethane (ethyl iodide)	6.83198	1175.709	225.26
1-Iodopropane	6.81603	1267.062	219.53
1-Iodobutane	6.82262	1358.860	214.20
1-Iodopentane	6.85172	1454.028	209.17
1-Iodohexane	6.8954	1549.17	204.55
1-Iodoheptane	6.9488	1644.29	200.25
1-Iodo-octane	7.0070	1738.53	196.23
1-Iodononane	7.0645	1830.37	192.5
1-Iododecane	7.1220	1919.75	188.9
1-Iodoundecane	7.1772	2006.28	185.5
1-Iodododecane	7.2290	2089.47	182.3
1-Iodotridecane	7.277	2169.2	179
1-Iodotetradecane	7.322	2245.4	176
1-Iodopentadecane	7.360	2318.3	174
1-Iodohexadecane	7.401	2388.0	171
1-Iodoheptadecane	7.437	2454.6	168
1-Iodo-octadecane	7.469	2518.7	166
1-Iodononadecane	7.498	2580.6	164
1-Iodoeicosane	7.524	2640.9	162

Table 23-9-2-(1.0111)-k.	C-F-H	1-Fluoroalkanes, C_1 to C_{10}
Table 23-9-2-(1.0112)-k.	C-F-H	1-Fluoroalkanes, C_{11} to C_{20}
Table 23-10-2-(1.0111)-k.	C-Cl-H.	1-Chloroalkanes, C_1 to C_{10}
Table 23-10-2-(1.0112)-k.	C-Cl-H.	1-Chloroalkanes, C_{11} to C_{20}
Table 23-11-2-(1.0111)-k.	C-Br-H.	1-Bromoalkanes, $C_1$to C_{10}
Table 23-11-2-(1.0112)-k.	C-Br-H.	1-Bromoalkanes, C_{11} to C_{20}
Table 23-12-2-(1.0111)-k.	C-I-H.	1-Iodoalkanes, C_1 to C_{10}
Table 23-12-2-(1.0112)-k.	C-I-H.	1-Iodoalkanes, C_{11} to C_{20}

These tables also give an indication of uncertainty in values of the calculated temperature for various pressures, the general rule being that the uncertainty in any of the values tabulated lies in the range of 2 to 15 units in the last place given. (The tables are available from the Manufacturing Chemists' Association, Washington 9, D. C.) Values of *A*, *B*, and *C* for members of these series beyond 20 carbon atoms, may be estimated from Figures 1, 2, and 3. For these, the uncertainties will of course be greater.

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