Vapor Pressures and Boiling Points of Normal Alkanes, C_{21} to C_{100}

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New empirical expressions based on existing experimental data are developed for the Antoine constants *B* and *C* in terms of the normal boiling point which together with the Kreglewski-Zwolinski equation for normal boiling points, are used to predict Antoine constants, vapor pressures, and boiling points for all 80 *n*-alkanes, C_{21} to C_{100}.

As part of a systematic program on the collection, analysis, calculation, correlation, and compilation of data on the physical and thermodynamic properties of hydrocarbons, the American Petroleum Institute Research Project 44 has investigated the data on vapor pressures for a large number of hydrocarbons, and compounds containing oxygen and sulfur. This paper presents a procedure for predicting vapor pressures and boiling points for *n*-alkanes in the carbon range, C_{21} to C_{100} (*2*).

The unavailability of high purity samples and the associated difficulties of experimental measurements have thwarted the determination of physical properties of high molecular weight alkanes beyond C_{20} although their properties are of great interest currently. Recently, Reinhard and Dixon (*7*) have successfully synthesized *n*-tetrananacontane ($C_{94}H_{190}$), and they have determined viscosities and densities of this hydrocarbon at three temperatures. No experimental vapor pressure and boiling points are available, however, for *n*-alkanes beyond carbon number $m = 36$ and one has to resort to empirical or semiempirical correlations for the prediction of their properties. Such a procedure based on extrapolation of existing experimental data is developed to predict the vapor pressure data of all *n*-alkanes, C_{21} to C_{100}.

Assuming the correctness of the Antoine equation for the higher molecular weight alkanes,

$$\log P = A - B/(C + t, ^\circ\text{C.}) \quad (1)$$

where P is in mm. of Hg, the authors have used Kreglewski and Zwolinski's approach (*5*) to develop the following power series expressions for the B and C constants in terms of the normal boiling point, T_b (° K.) based on the API Research Project 44 selected values for the C_3 to C_{17} *n*-alkanes:

$$\frac{B}{T_b} = 3.53813 - 9.77736 \times 10^{-5} T_b - 6.66695 \times 10^{-7} T_b^2 \quad (2)$$

$$\frac{C - 273.15}{T_b} = -4.49159 \times 10^{-2} - 2.68408 \times 10^{-4} T_b - 5.18608 \times 10^{-8} T_b^2 \quad (3)$$

To apply these relations, one additional relation is needed for predicting reliable values of the normal boiling points of the higher *n*-alkanes.

Recent studies by the authors (*8*) revealed that the Kreglewski-Zwolinski ($K - Z$) logarithmic expression (*4*), both on the basis of accuracy and ease of application, is to be preferred over the Li-Rossini expression for the higher carbon range only, C_{21} to C_{100}. The more rapid

Table I. Comparison with Experimental Boiling Points, ° C., of *n*-Alkanes (C_{20} to C_{36})

Carbon No., *m*	Boiling Points, ° C. At 5 mm. of Hg: Obs. (*1*)	Calcd.	Δt (calcd.-obs.)	At 10 mm. of Hg: Obs. (*1*)	Calcd.	Δt (calcd.-obs.)
20	181.0	181.3	+0.3	196.5	196.8	+0.3
23	212.5	211.6	−0.9	228.0	227.7	−0.3
24	220.5	220.9	+0.4	238.0	237.2	−0.8
26	240.0	238.6	−1.4	256.5	255.3	−1.2
28	255.5	255.1	−0.4	272.0	272.1	+0.1
32	284.0	284.9	+0.9	299.5	302.4	+2.9
35	300.0	304.9	+4.9	314.5	322.7	+8.2
36	311.0	311.1	+0.1	326.5	329.0	+2.5

Compound	Pressure, mm. of Hg	Calculated b.p., ° C.	Literature values
$C_{36}H_{54}$	1	205.	205.(*1*); 205.(*9*); 206.(*10*)
$C_{32}H_{66}$	11	305.	302[a].(*1*); 308.6(*10*); 311.(*11*)

[a] Extrapolated value from API Research Project 42 experimental data.

Table II. Antoine Constants and Boiling Points, ° C., of *n*-Alkanes (C_{21} to C_{100})

Formula	Description	Antoine Constants: *A*	*B*	*C*	B.P., ° C. at 760 mm. of Hg
$C_{21}H_{44}$	*n*-Heneicosane	7.0770	2022.5	125.5	356.5
$C_{22}H_{46}$	*n*-Docosane	7.0842	2054.0	120.1	368.6
$C_{23}H_{48}$	*n*-Tricosane	7.0911	2083.8	114.8	380.1
$C_{24}H_{50}$	*n*-Tetracosane	7.0976	2112.0	109.6	391.3
$C_{25}H_{52}$	*n*-Pentacosane	7.1038	2138.8	104.6	401.9
$C_{26}H_{54}$	*n*-Hexacosane	7.1096	2164.3	99.6	412.2
$C_{27}H_{56}$	*n*-Heptacosane	7.1152	2188.5	94.8	422.2
$C_{28}H_{58}$	*n*-Octacosane	7.1205	2211.6	90.0	431.6
$C_{29}H_{60}$	*n*-Nonacosane	7.1256	2233.6	85.4	440.8
$C_{30}H_{62}$	*n*-Triacontane	7.1304	2254.6	80.9	449.6
$C_{31}H_{64}$	*n*-Hentriacontane	7.1356	2276.9	75.9	459

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Table II. Antoine Constants and Boiling Points, ° C., of *n*-Alkanes (C_{21} to C_{100}) *(Continued)*

Formula	Description	Antoine Constants			B.P., ° C. at 760 mm. of Hg
		A	*B*	*C*	
$C_{32}H_{66}$	*n*-Dotriacontane	7.1400	2296.1	71.6	468
$C_{33}H_{68}$	*n*-Tritriacontane	7.1442	2314.4	67.3	476
$C_{34}H_{70}$	*n*-Tetratriacontane	7.1482	2331.9	63.1	483
$C_{35}H_{72}$	*n*-Pentatriacontane	7.1521	2348.6	59.1	491
$C_{36}H_{74}$	*n*-Hexatriacontane	7.1558	2364.6	55.1	498
$C_{37}H_{76}$	*n*-Heptatriacontane	7.1593	2380.0	51.2	505
$C_{38}H_{78}$	*n*-Octatriacontane	7.1627	2394.7	47.4	512
$C_{39}H_{80}$	*n*-Nonatriacontane	7.1660	2408.8	43.7	518
$C_{40}H_{82}$	*n*-Tetracontane	7.1691	2422.3	40.1	525
$C_{41}H_{84}$	*n*-Hentetracontane	7.1721	2435.3	36.5	531
$C_{42}H_{86}$	*n*-Dotetracontane	7.1750	2447.7	33.0	537
$C_{43}H_{88}$	*n*-Tritetracontane	7.1777	2459.7	29.6	543
$C_{44}H_{90}$	*n*-Tetratetracontane	7.1804	2471.2	26.3	548
$C_{45}H_{92}$	*n*-Pentatetracontane	7.1829	2482.3	23.0	554
$C_{46}H_{94}$	*n*-Hexatetracontane	7.1854	2493.0	19.8	559
$C_{47}H_{96}$	*n*-Heptatetracontane	7.1878	2503.3	16.7	565
$C_{48}H_{98}$	*n*-Octatetracontane	7.1900	2513.1	13.7	570
$C_{49}H_{100}$	*n*-Nonatetracontane	7.1922	2522.7	10.7	574
$C_{50}H_{102}$	*n*-Pentacontane	7.1944	2531.8	7.8	579
$C_{51}H_{104}$	*n*-Henpentacontane	7.1964	2540.7	4.9	584
$C_{52}H_{106}$	*n*-Dopentacontane	7.1984	2549.2	+2.1	588
$C_{53}H_{108}$	*n*-Tripentacontane	7.2003	2557.5	−0.7	593
$C_{54}H_{110}$	*n*-Tetrapentacontane	7.2021	2565.5	−3.3	597
$C_{55}H_{112}$	*n*-Pentapentacontane	7.2039	2573.1	−6.0	601
$C_{56}H_{114}$	*n*-Hexapentacontane	7.2056	2580.6	−8.5	605
$C_{57}H_{116}$	*n*-Heptapentacontane	7.2073	2587.7	−11.1	609
$C_{58}H_{118}$	*n*-Octapentacontane	7.2089	2594.7	−13.5	613
$C_{59}H_{120}$	*n*-Nonapentacontane	7.2104	2601.4	−16.0	617
$C_{60}H_{122}$	*n*-Hexacontane	7.2119	2607.9	−18.3	620
$C_{61}H_{124}$	*n*-Henhexacontane	7.2134	2614.2	−20.6	624
$C_{62}H_{126}$	*n*-Dohexacontane	7.2148	2620.2	−22.9	628
$C_{63}H_{128}$	*n*-Trihexacontane	7.2161	2626.1	−25.1	631
$C_{64}H_{130}$	*n*-Tetrahexacontane	7.2174	2631.8	−27.3	634
$C_{65}H_{132}$	*n*-Pentahexacontane	7.2187	2637.4	−29.5	637
$C_{66}H_{134}$	*n*-Hexahexacontane	7.2199	2642.7	−31.6	641
$C_{67}H_{136}$	*n*-Heptahexacontane	7.2211	2647.9	−33.6	644
$C_{68}H_{138}$	*n*-Octahexacontane	7.2223	2652.9	−35.6	647
$C_{69}H_{140}$	*n*-Nonahexacontane	7.2234	2657.8	−37.6	650
$C_{70}H_{142}$	*n*-Heptacontane	7.2245	2662.5	−39.5	653
$C_{71}H_{144}$	*n*-Henheptacontane	7.2256	2667.1	−41.4	655
$C_{72}H_{146}$	*n*-Doheptacontane	7.2266	2671.6	−43.3	658
$C_{73}H_{148}$	*n*-Triheptacontane	7.2276	2675.9	−45.1	661
$C_{74}H_{150}$	*n*-Tetraheptacontane	7.2286	2680.1	−46.9	663
$C_{75}H_{152}$	*n*-Pentaheptacontane	7.2295	2684.2	−48.7	666
$C_{76}H_{154}$	*n*-Hexaheptacontane	7.2304	2688.2	−50.4	668
$C_{77}H_{156}$	*n*-Heptaheptacontane	7.2313	2692.0	−52.1	671
$C_{78}H_{158}$	*n*-Octaheptacontane	7.2322	2695.8	−53.7	673
$C_{79}H_{160}$	*n*-Nonaheptacontane	7.2330	2699.4	−55.3	676
$C_{80}H_{162}$	*n*-Octacontane	7.2338	2702.9	−56.9	678
$C_{81}H_{164}$	*n*-Henoctacontane	7.2346	2706.4	−58.5	680
$C_{82}H_{166}$	*n*-Dooctacontane	7.2354	2709.7	−60.0	682
$C_{83}H_{168}$	*n*-Trioctacontane	7.2361	2713.0	−61.5	684
$C_{84}H_{170}$	*n*-Tetraoctacontane	7.2369	2716.2	−63.0	687
$C_{85}H_{172}$	*n*-Pentaoctacontane	7.2376	2719.2	−64.4	689
$C_{86}H_{174}$	*n*-Hexaoctacontane	7.2383	2722.2	−65.8	691
$C_{87}H_{176}$	*n*-Heptaoctacontane	7.2389	2725.2	−67.2	693
$C_{88}H_{178}$	*n*-Octaoctacontane	7.2396	2728.0	−68.6	694
$C_{89}H_{180}$	*n*-Nonaoctacontane	7.2402	2730.8	−69.9	696
$C_{90}H_{182}$	*n*-Nonacontane	7.2408	2733.5	−71.3	698
$C_{91}H_{184}$	*n*-Hennonacontane	7.2415	2736.1	−72.5	700
$C_{92}H_{186}$	*n*-Dononacontane	7.2420	2738.7	−73.8	702
$C_{93}H_{188}$	*n*-Trinonacontane	7.2426	2741.2	−75.1	704
$C_{94}H_{190}$	*n*-Tetranonacontane	7.2432	2743.6	−76.3	705
$C_{95}H_{192}$	*n*-Pentanonacontane	7.2437	2746.0	−77.5	707
$C_{96}H_{194}$	*n*-Hexanonacontane	7.2443	2748.3	−78.7	709
$C_{97}H_{196}$	*n*-Heptanonacontane	7.2448	2750.6	−79.8	710
$C_{98}H_{198}$	*n*-Octanonacontane	7.2453	2752.8	−80.9	712
$C_{99}H_{200}$	*n*-Nonanonacontane	7.2458	2755.0	−82.1	713
$C_{100}H_{202}$	*n*-Hectane	7.2463	2757.1	−83.1	715

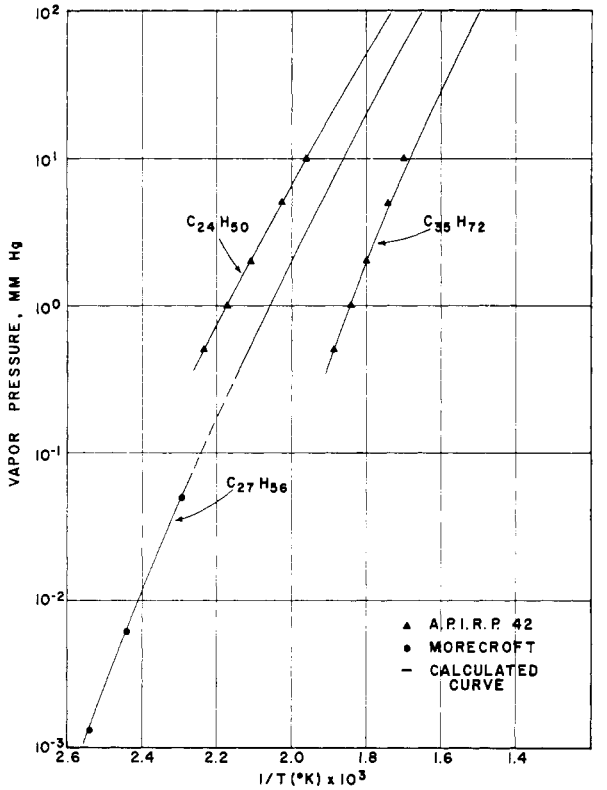

Figure 1. Comparison of predicted and experimental low pressure data for three normal alkanes

convergence of the *K-Z* relation beyond $m = 40$ is also in line with recent studies by Flory, Orwoll, and Vrij (*3*) for predicting the limiting value of T_b for $n = \infty$, namely, 1078°K. The following precise *K-Z* relation based on normal boiling points T_b (°K.), of *n*-alkanes in the range of $m = 6$ to 18 was used:

$$\log (1078 - T_b) = 3.03191 - 0.0499901\, m^{2/3} \qquad (4)$$

To test the soundness of the over-all procedure consisting of the above four relations for predicting the vapor pressure data of higher molecular weight *n*-alkanes, the Antoine constants *A*, *B*, and *C* were calculated using the four equations in the order 4, 2, 3, and 1. The predicted boiling points at 5 mm. and 10 mm. of Hg are compared with the experimental values for eight *n*-alkanes from API Research Project 42 (*1*) in Table I. The Antoine constants for these eight *n*-alkanes are given in Table II. A test of the procedure over a wider pressure range for three *n*-alkanes, C_{24}, C_{27}, and C_{35}, is given in Figure 1. The calculated vapor pressure curves as a function of absolute temperature are drawn through the experimental points of API Research Project 42 and Morecroft's values for $C_{27}H_{56}$ down to 10^{-3} mm. of Hg. Additional comparisons for some isolated determinations on $C_{26}H_{54}$ and $C_{32}H_{66}$ are given at the bottom of Table I. The agreement in all cases for the *n*-alkanes in the carbon range C_{20} to C_{36} is quite satisfactory and certainly recommends the use of this procedure for interpolation purposes. Since current studies on the composition and properties of higher molecular weight hydrocarbon fractions require property values for at least the basic *n*-alkanes, such estimated values should be made available by extrapolation of the procedure to at least the C_{100} value.

The convergence of the Kreglewski-Zwolinski correlation for the normal boiling points of *n*-alkanes in the carbon range of $m = 40$ to 100 also gives some assurance to the extension of this procedure for predicting boiling points and vapor pressures over the range 0.5 to 760 mm. of Hg for all higher *n*-alkanes above $m = 36$ for which no literature data are available. The predicted Antoine constants for all 80 *n*-alkanes in the carbon range C_{21} to C_{100} are summarized in Table II and can readily be used for calculating vapor pressures and boiling points for all the higher *n*-alkanes of interest. The normal boiling points at 760 mm. of Hg used in the correlation are given in the last column of Table II. Though for the most part fictitious, the t_b (°C.) listed are useful in various correlation procedures for other physical properties of alkanes. Use of these Antoine constants for extrapolations into the low pressure ranges too near the triple points is not recommended.

ACKNOWLEDGMENT

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