Article

New Method of NPOH Equation-Based to Estimate the Physicochemical Properties of Noncyclic Alkanes

Chao-Tun Cao and Chenzhong Cao*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Changes in various physicochemical properties ($P_{(n)}$) of noncyclic alkanes can be roughly classified as linear and nonlinear changes. In our previous study, the NPOH equation was proposed to express nonlinear changes in the properties of organic homologues. Until now, there has been no general equation to express nonlinear changes in the properties of noncyclic alkanes involving linear and branched alkane isomers. This work, on the basis of NPOH equation, proposes a general equation to express nonlinear changes in the physicochemical properties of noncyclic alkanes, including a total of 12 properties, boiling point, critical temperature, critical pressure, acentric factor, heat capacity, liquid viscosity, and flash point, named as the "NPNA equation", as follows: $\ln(P_{(n)}) = a + b(n - 1) + c(S_{CNE}) + d(\Delta AOEI) + f(\Delta AIMPI)$, where a, b, c, and f are coefficients, and $P_{(n)}$ represents the property of the alkane with n carbon atom number. n, S_{CNE}, $\Delta AOEI$, and $\Delta AIMPI$ are number of carbon atoms, sum of carbon number effects, average odd−even index difference, and average inner molecular polarizability index difference, respectively. The obtained results show that various nonlinear changes in the properties of noncyclic alkanes can be expressed by the NPNA equation. Nonlinear and linear change properties of noncyclic alkanes can be correlated with four parameters, n, S_{CNE}, $\Delta AOEI$, and $\Delta AIMPI$. The NPNA equation has the advantages of uniform expression, usage of fewer parameters, and high estimation accuracy. Furthermore, using the above four parameters, a quantitative correlation equation can be established between any two properties of noncyclic alkanes. Employing the obtained equations as model equations, the property data of noncyclic alkanes, involving 142 critical temperatures, 142 critical pressures, 115 acentric factors, 116 flash points, 174 heat capacities, 142 critical volumes, and 155 gas enthalpies of formation, a total of 986 values, were predicted, which have not be experimentally measured. NPNA equation not only can provide a simple and convenient estimation or prediction method for the properties of noncyclic alkanes but also can provide new perspectives for studying quantitative structure−property relationships of branched organic compounds.

Linear/branched alkanes C_nH_{2n+2}

$\ln(P_{(n)}) = a + b(n-1) + c(S_{CNE}) + d(\Delta AOEI) + f(\Delta AIMPI)$
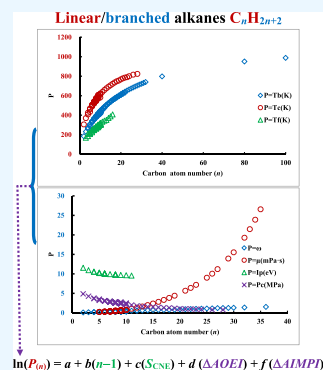
1. INTRODUCTION

Alkanes are important compounds and are widely used in various industrial processes, such as energy, fuel, and petrochemical industry. Their physicochemical propery data are indispensable basic data in chemical production, scientific research, and practical application. Due to the huge number of isomers of alkanes, determining the physicochemical properties of all compounds experimentally is an impossible task, so it is very meaningful to establish an estimation method. Until now, people have gradually established many valuable estimation methods,[1−95] such as (i) group-contribution (GC) methods,[4,9,18,37,54,55,70,86] (ii) estimating one physicochemical property from that of other compounds,[1,2,8,14,16,17,19,20,22,24,36,39,45,48,57,64−66,74,75,78,85,89] (iii) liquid equations of states (EoS)-based methods,[3,5,7,11,13,21,25,26,31,34,40,41,46,47,49−51,53,61,88,90−92] and (iv) quantitative structure−property relationships (QSPRs).[15,30,38,42,44,52,56,59,60,67−69,71−73,77,80−82,87,93,94] Using the above methods, many estimation equations are obtained for estimating various physicochemical properties of alkanes (pure compounds or mixture systems).[1−94] These properties involve the boiling point (T_b), critical temperature (T_c), critical pressure (P_c), acentric factor (ω), heat capacity (C_p), enthalpy of formation ($\Delta_f H°$), enthalpy of vaporization (H_v), and vapor pressure (P_v), and so on. Here are some examples.
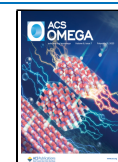
GC methods (i) can be expressed by eq 1[95]

$$Y = \left(\sum_i A_i B_i\right)^a + \left(\sum_j C_j D_j\right)^b + \left(\sum_k E_k F_k\right)^c \quad (1)$$

GC methods are generally easy to use, in which one property Y of a compound can be estimated by a sum of terms or contributions (the A_i to F_k values) representing the different groups present in a molecule. The linear or nonlinear character of eq 1 is determined by the constants a, b, and c.

He et al.[4] proposed eqs 2 and 3 to estimate T_c and P_c, respectively

$$T_c = T_b / (a_1 + a_2 T_g + a_3 T_g^2 + a_4 T_g^3) + w T_s \qquad (2)$$

$$P_c = \ln T_b / (a_5 + a_6 P_g + a_7 P_g^2 + a_8 P_g^3 + w P_s) \qquad (3)$$

In eqs 2 and 3, the a_1, a_2, ..., and a_8 are coefficients, T_g and P_g are the first-level group contributions, and T_s and P_s are the second-level group contributions. If only the contribution of the first-level group is used, $w = 0$; both the first- and second-level group contributions are included, $w = 1$.

Wang et al.[55] used eq 4 to predict the ω of organic compounds and obtained good results

$$\omega = 7.86948 + \Sigma_i A_i N_i + \Sigma_j A_j \ \tanh(N_j / N) + \Sigma_k A_k P_k$$
$$- 7.62035 \ \exp(1 / M) + 0.025051 \ \exp(1 / N) \qquad (4)$$

In eq 4

$$N = \Sigma_i N_i + \Sigma_j N_j \qquad (5)$$

Hukkerikar et al.[37] used group-contribution+ (GC+) to estimate properties of pure components of various classes (hydrocarbons, oxygenated components, nitrogenated components, etc.).

Method (ii) is by using the easy-to-measure properties to estimate the difficult-to-measure properties via employing some empirical equations.

Gamba et al.[51] used T_b of alkanes to estimate their T_c, as shown in eq 6

$$\ln(b_1 - T_c) = b_2 \ \ln(b_4 - T_b) - b_3 \qquad (6)$$

where b_1, b_2, b_3, and b_4 are coefficients.

Gamba et al.[51] proposed eqs 7 and 8 to estimate the acentric factors (ω) of paraffins

$$\ln(1187.9291 - \omega) = 8.9643355 \times 10^{-4} \ \ln(1004.8417$$
$$- T_b / K) + 7.0738919 \qquad (7)$$

$$\ln(1185.0931 - \omega) = 1.0478687 \times 10^{-3} \ \ln(1047.5707$$
$$- T_b / K) + 7.0704986 \qquad (8)$$

Equations 7 and 8 are used in different range of boiling points T_b, respectively.

The typical equation of method (iii) is the cubic state eq 9.[95] However, Wilhelmsen et al.[96] pointed out: "EoS are essential in the modeling of a wide range of industrial and natural processes. Desired qualities of EoS are accuracy, consistency, computational speed, robustness, and predictive ability outside of the domain where they have been fitted"

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + uVb + wb^2} \qquad (9)$$

In eq 9, u and w are characteristics of the equation, and the a and b are calculated by eqs 10 and 11, respectively

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T) \qquad (10)$$

$$b = \Omega_b \frac{R T_c}{P_c} \qquad (11)$$

The QSPR method (iv) correlates an experimental property of compounds with a series of molecular descriptors. It can be expressed as the following general form[95]

$$\text{property} = f(\text{descriptors}) \qquad (12)$$

In eq 12, different descriptors (involving constitutional, topological, geometric, and quantum chemical) are employed to characterize the molecular structures of the interested compounds.

Palatinus et al.[97] proposed eq 13 for calculating the Y_R parameter and then employed the obtained Y_R values and eq 14 to estimate the boiling points for linear and branched alkanes

$$Y_R = 1.726 + 2.779C + 1.716M_3 + 1.564M + 4.204E_3$$
$$+ 3.905E + 5.007P$$
$$- 0.329D + 0.241G + 0.479V + 0.967T + 0.574S \qquad (13)$$

$$T_b \ (K) = a Y_{BP}^{2/3} + b Y_{BP}^{1/3} + c \qquad (14)$$

In eq 13, C is the number of carbon atoms in the longest carbon chain; M is the count of methyl groups (M_3 for 3-methyl); E is the count of ethyl groups (E_3 for 3-ethyl); G is all other geminal disubstitutions; P is the number of propyl groups. D is a specific parameter for 2,2-dimethyl substitution; V is the total count of vicinal alkyl relationships; T is the number of groupings with two methyl substituents on both carbons 1 and 3 of a three-carbon segment of the main chain; S is the square of the ratio of the total number of carbons to the number of carbons in the longest chain.

Mukwembi et al.,[98] recently, proposed parameter $c(G)$ for predicting the T_b of any given alkane and obtained good results. Yuan and Cao.[99] used eq 15 to correlate the vapor pressure of hydrocarbons

$$\log P_v = 8.0183 - 0.6040n^{2/3} + 0.2013VDI - 0.2377OEI$$
$$- 0.1992EDI + 0.0763S_e \qquad (15)$$

In eq 15, the n is carbon atom number, VDI, OEI, EDI, and S_e are topological indices.

It can be seen from the abovementioned facts that there are various methods for estimating the physicochemical properties of alkanes, and the equation forms are different, that is, different estimation equations need to be used for different properties. Then, it is a very meaningful subject whether the changes of different physicochemical properties of a same kind of organic compounds (such as alkanes) can be expressed by a same type equation. The solution of this subject will provide great convenience for the estimation of the properties of organic compounds.

Kontogeorgis,[100] in 2021, pointed out that companies ideally wish for predictive models validated on extensive experimental databases and not only on just a few available experimental data points. To study this challenge, we recently proposed NPOH equation to express various nonlinear changes in the properties of homologues and observed that the linear and nonlinear changes in the properties of homologues can all be correlated with carbon atom number n and the "sum of carbon number effects," S_{CNE}, and pointed out: "for nonstraight-chain isomers, using the NPOH equation, we can add structural parameters that characterize the molecular carbon atomic skeleton to establish an estimation model for their properties."[101] In this work, we try to establish a general equation expressing nonlinear

changes in the physicochemical properties of nonstraight-chain alkanes.

2. RESULTS AND DISCUSSION

2.1. Theoretical Analysis. The result of our previous study[101] shows that the changes in physicochemical properties of n-paraffin homologues ($H-(CH_2)_n-H$) can be expressed by only employing parameters n and S_{CNE}. However, for the
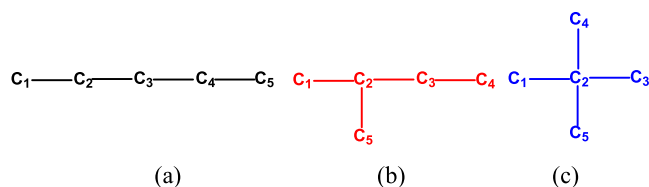
Figure 1. Molecular carbon atomic skeleton diagram of (a) n-pentane, (b) 2-methylbutane, and (c) 2,2-dimethylpropane (numbers indicate carbon atom number).

isomers containing n carbon atoms, such as n-pentane $H-(CH_2)_5-H$, 2-methylbutane $(CH_3)_2CHCH_2CH_3$ and 2,2-dimethylpropane $CH_3C(CH_3)_2CH_3$, they have the same number of carbon atoms, but they are constitutional isomers and have different molecular carbon atomic skeletons. Therefore, the changes in physicochemical properties of branched alkane isomers are not only related to the parameters n and S_{CNE} but also related to the difference in the molecular carbon atomic skeleton of branched and linear alkanes. We noticed that many topological indices were proposed to express the molecular carbon atomic skeleton of alkane molecules. In this study, the odd−even index (OEI)[102] and the inner molecular polarization index (IMPI)[103] were selected to express the difference of carbon atomic skeleton between branched and linear alkanes.

2.1.1. Calculation of OEI and IMPI of Alkanes. Take pentane (C_5H_{12}), for example, it has three isomers, as shown in Figure 1. The calculations of OEI and IMPI values of these isomers are restated briefly as follows:

① Odd−even Index (OEI)

$$OEI = \sum_{i=1}^{n} \sum_{j \neq i}^{n} [(-1)^{D_{ij}-1} S] \tag{16}$$

where n is the number of vertices (carbon atoms) in molecular graph. S is the derivative matrix from distance matrix D. The elements of S are the squares of the reciprocal distances $(D_{ij})^{-2}$, i.e., $S_{ij} = 1/D_{ij}^2$ (when $i = j$, let $1/D_{ij}^2 = 0$).

The distance matrix $D(a)$, $D(b)$, and $D(c)$ of (a), (b), and (c) in Figure 1, and their derivative matrix $S(a)$, $S(b)$, $S(c)$ are as follows, respectively

$$D(a) = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 \\ 1 & 0 & 1 & 2 & 3 \\ 2 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 0 & 1 \\ 4 & 3 & 2 & 1 & 0 \end{bmatrix} \quad D(b) = \begin{bmatrix} 0 & 1 & 2 & 3 & 2 \\ 1 & 0 & 1 & 2 & 1 \\ 2 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 0 & 3 \\ 2 & 1 & 2 & 3 & 0 \end{bmatrix}$$

$$D(c) = \begin{bmatrix} 0 & 1 & 2 & 2 & 2 \\ 1 & 0 & 1 & 1 & 1 \\ 2 & 1 & 0 & 2 & 2 \\ 2 & 1 & 2 & 0 & 2 \\ 2 & 1 & 2 & 2 & 0 \end{bmatrix}$$

Table 1. PEI and ΔPEI Values of Linear Alkyl $H(CH_2)_n-$

n	PEI	n_i	ΔPEI	n	PEI	n_i	ΔPEI	n	PEI	n_i	ΔPEI	n	PEI	n_i	ΔPEI
1	1.0000	1	1.00000	26	1.2686	26	0.00039	51	1.2734	51	0.00010	76	1.2750	76	0.00004
2	1.1405	2	0.14053	27	1.2690	27	0.00036	52	1.2735	52	0.00009	77	1.2750	77	0.00004
3	1.1887	3	0.04813	28	1.2693	28	0.00034	53	1.2736	53	0.00009	78	1.2751	78	0.00004
4	1.2122	4	0.02350	29	1.2696	29	0.00031	54	1.2737	54	0.00009	79	1.2751	79	0.00004
5	1.2260	5	0.01380	30	1.2699	30	0.00029	55	1.2737	55	0.00008	80	1.2752	80	0.00004
6	1.2350	6	0.00905	31	1.2702	31	0.00027	56	1.2738	56	0.00008	81	1.2752	81	0.00004
7	1.2414	7	0.00639	32	1.2704	32	0.00026	57	1.2739	57	0.00008	82	1.2752	82	0.00004
8	1.2461	8	0.00475	33	1.2707	33	0.00024	58	1.2740	58	0.00008	83	1.2753	83	0.00004
9	1.2498	9	0.00367	34	1.2709	34	0.00023	59	1.2741	59	0.00007	84	1.2753	84	0.00004
10	1.2527	10	0.00292	35	1.2711	35	0.00021	60	1.2741	60	0.00007	85	1.2754	85	0.00004
11	1.2551	11	0.00238	36	1.2713	36	0.00020	61	1.2742	61	0.00007	86	1.2754	86	0.00003
12	1.2571	12	0.00197	37	1.2715	37	0.00019	62	1.2743	62	0.00007	87	1.2754	87	0.00003
13	1.2587	13	0.00166	38	1.2717	38	0.00018	63	1.2743	63	0.00006	88	1.2755	88	0.00003
14	1.2602	14	0.00142	39	1.2719	39	0.00017	64	1.2744	64	0.00006	89	1.2755	89	0.00003
15	1.2614	15	0.00123	40	1.2720	40	0.00016	65	1.2744	65	0.00006	90	1.2755	90	0.00003
16	1.2625	16	0.00107	41	1.2722	41	0.00015	66	1.2745	66	0.00006	91	1.2755	91	0.00003
17	1.2634	17	0.00094	42	1.2723	42	0.00015	67	1.2746	67	0.00006	92	1.2756	92	0.00003
18	1.2642	18	0.00084	43	1.2725	43	0.00014	68	1.2746	68	0.00006	93	1.2756	93	0.00003
19	1.2650	19	0.00075	44	1.2726	44	0.00013	69	1.2747	69	0.00005	94	1.2756	94	0.00003
20	1.2657	20	0.00067	45	1.2727	45	0.00013	70	1.2747	70	0.00005	95	1.2757	95	0.00003
21	1.2663	21	0.00061	46	1.2728	46	0.00012	71	1.2748	71	0.00005	96	1.2757	96	0.00003
22	1.2668	22	0.00055	47	1.2730	47	0.00012	72	1.2748	72	0.00005	97	1.2757	97	0.00003
23	1.2673	23	0.00050	48	1.2731	48	0.00011	73	1.2749	73	0.00005	98	1.2757	98	0.00003
24	1.2678	24	0.00046	49	1.2732	49	0.00011	74	1.2749	74	0.00005	99	1.2758	99	0.00003
25	1.2682	25	0.00042	50	1.2733	50	0.00010	75	1.2750	75	0.00005	100	1.2758	100	0.00003

Table 2. CAS Registry Number, OEI and IMPI Values of 149 Alkane Molecules Bearing 2 to 10 Carbon Atoms

no	alkanes	n^a	$CASN^b$	OEI	IMPI
1	ethane	2	74-84-0	2.0000	2.0000
2	propane	3	74-98-6	3.5000	4.2811
3	2-methylpropane	4	75-28-5	4.5000	6.8432
4	butane	4	106-97-8	5.2222	6.6584
5	2,2-dimethylpropane	5	463-82-1	5.0000	9.6863
6	2-methylbutane	5	78-78-4	6.4444	9.3167
7	pentane	5	109-66-0	6.8194	9.0827
8	2,2-dimethylbutane	6	75-83-2	7.1667	12.2562
9	2,3-dimethylbutane	6	79-29-8	7.8889	12.0708
10	2-methylpentane	6	107-83-5	7.9167	11.7881
11	3-methylpentane	6	96-14-0	8.2639	11.8373
12	hexane	6	110-54-3	8.4967	11.5345
13	2,2,3-trimethylbutane	7	464-06-2	8.8333	15.1071
14	2,2-dimethylpentane	7	590-35-2	8.5139	14.7745
15	3,3-dimethylpentane	7	562-49-2	9.2083	14.8730
16	2,3-dimethylpentane	7	565-59-3	9.5833	14.6390
17	2,4-dimethylpentane	7	108-08-7	8.8889	14.5404
18	2-methylhexane	7	591-76-4	9.6739	14.2676
19	3-methylhexane	7	589-34-4	9.8161	14.3360
20	3-ethylpentane	7	617-78-7	9.9583	14.4049
21	heptane	7	142-82-5	10.1183	14.0046
22	2,2,3,3-tetramethylbutane	8	594-82-1	10.0000	18.2390
23	2,2,3-trimethylpentane	8	564-02-3	10.4028	17.7217
24	2,3,3-trimethylpentane	8	560-21-4	10.7500	17.8190
25	2,2,4-trimethylpentane	8	540-84-1	9.3611	17.5739
26	2,2-dimethylhexane	8	590-73-8	10.3511	17.2816
27	3,3-dimethylhexane	8	563-16-6	10.6356	17.4189
28	3-ethyl-3-methylpentane	8	1067-08-9	11.1250	17.4369
29	2,3,4-trimethylpentane	8	565-75-3	10.7778	17.4865
30	2,3-dimethylhexane	8	584-94-1	11.2156	17.1655
31	3-ethyl-2-methylpentane	8	609-26-7	11.1528	17.2536
32	3,4-dimethylhexane	8	583-48-2	11.3578	17.2342
33	2,4-dimethylhexane	8	589-43-5	10.8683	17.1162
34	2,5-dimethylhexane	8	592-13-2	10.9311	17.0282
35	2-methylheptane	8	592-27-8	11.2400	16.7557
36	3-methylheptane	8	589-81-1	11.5178	16.8339
37	4-methylheptane	8	589-53-7	11.3128	16.8533
38	3-ethylhexane	8	619-99-8	11.5906	16.9314
39	octane	8	111-65-9	11.7808	16.4874
40	2,2,3,3-tetramethylpentane	9	7154-79-2	11.7917	20.9499
41	2,2,3,4-tetramethylpentane	9	1186-53-4	11.4722	20.6173
42	2,2,3-trimethylhexane	9	16747-25-4	12.1150	20.2758
43	2,2-dimethyl-3-ethylpentane	9	16747-32-3	11.8472	20.5277
75	2,2,3,3,4-pentamethylpentane	10	16747-44-7	13.0833	23.9418
76	2,2,3,3-tetramethylhexane	10	13475-81-5	13.3789	23.5510
77	3-ethyl-2,2,3-trimethylpentane	10	52897-17-3	13.4583	23.7077
78	3,3,4,4-tetramethylhexane	10	5171-84-6	13.6633	23.6883
79	2,2,3,4,4-pentamethylpentane	10	16747-45-8	12.0417	23.6530
80	2,2,3,4-tetramethylhexane	10	52897-08-2	13.4067	23.2677
81	3-ethyl-2,2,4-trimethylpentane	10	52897-18-4	12.7917	23.3259
82	2,3,4,4-tetramethylhexane	10	52897-12-8	13.5489	23.3364
83	2,2,3,5-tetramethylhexane	10	52897-09-3	13.3272	22.8580
84	2,2,3-trimethylheptane	10	52896-92-1	13.7056	22.8096
85	2,2-dimethyl-3-ethylhexane	10	20291-91-2	13.6394	23.1094
86	3,3,4-trimethylheptane	10	20278-87-9	14.0561	22.9853
87	3,3-dimethyl-4-ethylhexane	10	52897-05-9	13.9239	23.1023
88	2,3,3,4-tetramethylhexane	10	52897-10-6	13.8961	23.3870
89	3,4,4-trimethylheptane	10	20278-88-0	13.8511	23.0047
90	3,4-dimethyl-3-ethylhexane	10	52897-06-0	14.2711	23.1516
91	3-ethyl-2,3,4-trimethylpentane	10	52897-19-5	13.8333	23.4757
92	2,3,3,5-tetramethylhexane	10	52897-11-7	13.2644	23.1990
93	2,3,3-trimethylheptane	10	16747-28-7	13.9833	22.8878
94	2,3-dimethyl-3-ethylhexane	10	52897-00-4	15.0178	23.0829
95	3,3-diethyl-2-methylpentane	10	52897-16-2	14.2083	23.2396
96	2,2,4,4-tetramethylhexane	10	51750-65-3	11.9900	23.2129
97	2,2,4,5-tetramethylhexane	10	16747-42-5	12.9800	23.0617
98	2,2,4-trimethylheptane	10	14720-74-2	12.8061	22.7305
99	2,2-dimethyl-4-ethylhexane	10	52896-99-8	13.3550	22.8277
100	3,3,5-trimethylheptane	10	7154-80-5	13.5667	22.8868
101	2,4,4-trimethylheptane	10	4032-92-2	12.8789	22.8281
102	2,4-diethyl-4-ethylhexane	10	52897-03-7	13.6394	22.9650
103	2,2,5,5-tetramethylhexane	10	1071-81-4	12.5256	23.1391
104	2,2,5-trimethylheptane	10	20291-95-6	13.4211	22.6724
105	2,5,5-trimethylheptane	10	1189-99-7	13.6989	22.7504
106	2,2,6-trimethylheptane	10	1190-83-6	12.8722	22.5752
107	2,2-dimethyloctane	10	15869-87-1	13.6058	22.2962
108	3,3-dimethyloctane	10	4110-44-5	13.9686	22.4632
109	4,4-dimethyloctane	10	15869-95-1	13.8297	22.5210
110	3-ethyl-3-methylheptane	10	17302-01-1	14.3583	22.6537
111	4-ethyl-4-methylheptane	10	17302-04-4	14.0839	22.7020
112	3,3-diethylhexane	10	17302-02-2	14.5039	22.8489
113	2,3,4,5-tetramethylhexane	10	52897-15-1	13.9867	22.9016
114	2,3,4-trimethylheptane	10	52896-95-4	14.1533	22.5605
115	2,3-dimethyl-4-ethylhexane	10	52897-01-5	14.3617	22.6675
116	2,4-dimethyl-3-ethylhexane	10	7220-26-0	14.1567	22.6869
117	3,4,5-trimethylheptane	10	20278-89-1	14.4311	22.6386

Table 2. continued

no	alkanes	n^a	CASN^b	OEI	IMPI
44	3,3,4-trimethylhexane	9	16747-31-2	12.3994	20.4131
45	2,3,3,4-tetramethylpentane	9	16747-38-9	12.1667	20.7172
46	2,3,3-trimethylhexane	9	16747-28-7	12.2572	20.3444
47	2,3-dimethyl-3-ethylpentane	9	16747-33-4	12.5417	20.4837
48	2,2,4,4-tetramethylpentane	9	1070-87-7	9.7083	20.5133
49	2,2,4-trimethylhexane	9	16747-26-5	11.4206	20.1773
50	2,4,4-trimethylhexane	9	16747-30-1	11.5628	20.2459
51	2,2,5-trimethylhexane	9	3522-94-9	11.6883	20.0698
52	2,2-dimethylheptane	9	1071-26-7	11.8617	19.7848
53	3,3-dimethylheptane	9	4032-86-4	12.4172	19.9442
54	4,4-dimethylheptane	9	1068-19-5	12.0072	19.9830
55	3-ethyl-3-methylhexane	9	3074-76-8	12.6322	20.1104
56	3,3-diethylpentane	9	1067-20-5	12.9167	20.2477
57	2,3,4-trimethylhexane	9	921-47-1	12.6322	19.9977
58	2,4-dimethyl-3-ethylpentane	9	1068-87-7	12.2222	20.1493
59	2,3,5-trimethylhexane	9	1069-53-0	12.3478	19.9328
60	2,3-dimethylheptane	9	3074-71-3	12.8617	19.6812
61	3-ethyl-2-methylhexane	9	16789-46-1	12.8650	19.8076
62	3,4-dimethylheptane	9	922-28-1	12.9344	19.7307
63	3-ethyl-4-methylhexane	9	3074-77-9	13.0072	19.7842
64	2,4-dimethylheptane	9	2213-23-2	12.3094	19.6514
65	4-ethyl-2-methylhexane	9	3074-75-7	12.7228	19.7390
66	3,5-dimethylheptane	9	926-82-9	12.7922	19.7101
67	2,5-dimethylheptane	9	2216-30-0	12.7194	19.6126
68	2,6-dimethylheptane	9	1072-05-5	12.3061	19.5250
69	2-methyloctane	9	3221-61-2	12.9433	19.2513
70	3-methyloctane	9	2216-33-3	13.1247	19.3348
71	4-methyloctane	9	2216-34-4	13.0553	19.3637
72	3-ethylheptane	9	15869-80-4	13.2367	19.4472
73	4-ethylheptane	9	2216-32-2	13.1672	19.4760
74	nonane	9	111-84-2	13.4120	18.9797
118	2,4-dimethyl-3-isopropylpentane	10	13475-79-1	13.1667	23.0920
119	3-isopropyl-2-methylhexane	10	62016-13-1	14.0144	22.7309
120	2,3,5-trimethylheptane	10	20278-85-7	14.2161	22.5851
121	2,5-dimethyl-3-ethylhexane	10	52897-04-8	14.0772	22.6429
122	2,4,5-trimethylheptane	10	20278-84-6	14.0111	22.6045
123	2,3,6-trimethylheptane	10	4032-93-3	14.0078	22.4780
124	2,3-dimethyloctane	10	7146-60-3	14.5094	22.1949
125	3-ethyl-2-methylheptane	10	14676-29-0	14.4556	22.3415
126	3,4-dimethyloctane	10	15869-92-8	14.6214	22.3073
127	4-isopropylheptane	10	52896-87-4	14.5217	22.3799
128	4-ethyl-3-methylheptane	10	52896-89-6	14.6639	22.4005
129	4,5-dimethyloctane	10	15869-96-2	14.5519	22.3362
130	3-ethyl-4-methylheptane	10	15869-91-0	14.5283	22.4391
131	3,4-diethylhexane	10	19398-77-7	14.7367	22.4540
132	2,4,6-trimethylheptane	10	2613-61-8	13.2506	22.4676
133	2,4-dimethyloctane	10	4032-94-4	14.0927	22.1745
134	4-ethyl-2-methylheptane	10	52896-90-9	14.2439	22.3018
135	3,5-dimethyloctane	10	15869-93-9	14.2741	22.2580
136	3-ethyl-5-methylheptane	10	52896-88-5	14.5911	22.3510
137	2,5-dimethyloctane	10	15869-89-3	14.2977	22.1551
138	5-ethyl-2-methylheptane	10	13475-78-0	14.3828	22.2440
139	3,6-dimethyloctane	10	15869-94-0	14.5486	22.2097
140	2,6-dimethyloctane	10	2051-30-1	14.2316	22.1168
141	2,7-dimethyloctane	10	1072-16-8	14.1466	22.0279
142	2-methylnonane	10	871-83-0	14.5433	21.7531
143	3-methylnonane	10	5911-04-6	14.7968	21.8399
144	4-methylnonane	10	17301-94-9	14.6309	21.8741
145	3-ethyloctane	10	5881-17-4	14.8844	21.9609
146	5-methylnonane	10	15869-85-9	14.7665	21.8836
147	4-ethyloctane	10	15869-86-0	14.8541	22.0046
148	4-propylheptane	10	3178-29-8	14.6883	22.0388
149	decane	10	124-18-5	15.0680	21.4794

^{a}Carbon atom number. ^{b}CAS registry number.

Table 3. Correlation Equations of Nonlinear Change Properties for Noncyclic Alkanes (C_nH_{2n+2}) (Model Equation: $\ln(P_{(n)}) = a + b(n-1) + c(S_{CNE}) + d(\Delta AOEI) + f(\Delta AIMPI)$)

no	property[a]	range of n[b]	refs	A	b	c	d	f	R[c]	S[c]	N[c]	F[c]
1	T_b	2–100	103	4.6711	−0.004557	0.51642	0.23933	0.07237	0.9991	0.0092	210	28909.97
2	T_c	2–28	104	5.2970	−0.008300	0.42350	0.27253	0.28032	0.9989	0.0090	66	7024.25
3	P_c	2–28	104	1.9947	−0.041536	−0.30826	0.38453	1.12759	0.9981	0.0257	66	4100.30
4	ω	2–36	55	−3.2295	−0.001719	0.89336	0.06814	−1.78074	0.9988	0.0258	93	9534.25
5	D	5–17	102	−0.9705	−0.008948	0.25682	0.24878	0.55096	0.9315	0.0178	61	91.80
6	C_p	4–16	102	3.6320	0.025742	0.66599	0.06886	−0.17736	0.9993	0.0101	34	5516.54
7	n_D	4–20	102	0.1752	−0.002361	0.06646	0.05358	0.11829	0.9414	0.00422	150	282.38
8	P_v	2–16	102	7.3280	−0.455149	−0.32903	−1.04425	1.67722	0.9958	0.0121	63	1711.36
9	I_p	2–11	104	2.5643	0.004886	−0.12107	0.02298	0.01648	0.9980	0.0033	20	912.82
10	S_w	2–10	105	3.5869	0.867740	−1.73424	0.06906	−2.85871	0.9931	0.1209	24	341.51
11	μ	5–35	106	−5.1254	0.066700	1.50894	−0.51913	−0.10828	0.9960	0.1174	78	2254.46
12	T_F	3–16	93	4.4741	0.003817	0.44150	0.14294	−0.13321	0.9923	0.0172	92	1398.31

[a]T_b, normal boiling point (K); T_c, critical temperature (K); P_c, critical pressure (MPa); ω, acentric factor; D, liquid density (g·cm^{-3}, 293.15 K); C_p, heat capacity (J·mol^{-1}·K^{-1}); n_D, refractive index (293.15 K); P_v, vapor pressure (Pa, 298.15 K), regression in the form of log P_v; I_p, ionization potential (eV); S_w, water solubility (mol·L^{-1}, 298.15 K), regression in the form of −log S_w; μ, liquid viscosity[mPa·s (300 K)]; T_F, flash point (K). These properties data are listed in the Supporting Information. [b]Carbon atom number range. [c]R, S, N, and F are correlation coefficient, standard error, number of data points, and Fisher test, respectively.

$$S(a) = \begin{bmatrix} 0 & 1/1 & 1/4 & 1/9 & 1/16 \\ 1/1 & 0 & 1/1 & 1/4 & 1/9 \\ 1/4 & 1/1 & 0 & 1/1 & 1/4 \\ 1/9 & 1/4 & 1/1 & 0 & 1/1 \\ 1/16 & 1/9 & 1/4 & 1/1 & 0 \end{bmatrix}$$

$$S(b) = \begin{bmatrix} 0 & 1/1 & 1/4 & 1/9 & 1/4 \\ 1/1 & 0 & 1/1 & 1/4 & 1/1 \\ 1/4 & 1/1 & 0 & 1/1 & 1/4 \\ 1/9 & 1/4 & 1/1 & 0 & 1/9 \\ 1/4 & 1/1 & 1/4 & 1/9 & 0 \end{bmatrix}$$

$$S(c) = \begin{bmatrix} 0 & 1/1 & 1/4 & 1/4 & 1/4 \\ 1/1 & 0 & 1/1 & 1/1 & 1/1 \\ 1/4 & 1/1 & 0 & 1/4 & 1/4 \\ 1/4 & 1/1 & 1/4 & 0 & 1/4 \\ 1/4 & 1/1 & 1/4 & 1/4 & 0 \end{bmatrix}$$

Using eq 16, the OEI values of (a), (b), and (c) in Figure 1 are calculated as follows

OEI(a) = $1 \times 8 + (-1/4) \times 6 + (1/9) \times 4$
$+ (-1/16) \times 2 = 6.8194$

OEI(b) = $1 \times 8 + (-1/4) \times 8 + (1/9) \times 4 = 6.4444$

OEI(c) = $1 \times 8 + (-1/4) \times 12 = 5.0000$

It shows that the OEI values of *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane are 6.8194, 6.4444, and 5.0000, respectively.

② Inner molecular polarizability index (IMPI)

$$IMPI = \Sigma PEI(i) \qquad (17)$$

In eq 17, the PEI(i) is the sum of the polarizability effect index of alkyl groups (R_i) connected to the ith carbon atom, that is, the ith carbon atom in an alkane molecule was taken as the beginning atom, the other part was taken as the alkyl group. The

PEI(i) value of alkyl group R_i can be calculated with the ΔPEI values of carbon atoms in R_i (see Table 1), that is, PEI(i) = $\Sigma\Delta$PEI(i). Take Figure 1a, for example, the C_1 connects with a butyl, the C_2 connects with a methyl and a propyl, and the C_3 connects with two ethyl.

The calculations of IMPI of Figure 1a−c, for examples, are described as follows

IMPI(a)

C_1 : PEI(1) = $1.00000 + 0.14053 + 0.04813 + 0.02350$
$= 1.21216$

C_2 : PEI(2) = $2 \times 1.00000 + 0.14053 + 0.04813$
$= 2.18866$

C_3 : PEI(3) = $2 \times 1.00000 + 2 \times 0.14053 = 2.28106$

C_4 : PEI(4) = $2 \times 1.00000 + 0.14053 + 0.04813$
$= 2.18866$

C_5 : PEI(5) = $1.00000 + 0.14053 + 0.04813 + 0.02350$
$= 1.21216$

IMPI(a) = ΣPEI(i) = $1.21216 + 2.18866 + 2.28106$
$+ 2.18866 + 1.21216 = 9.0827$

IMPI(b)

C_1 : PEI(1) = $1.00000 + 2 \times 0.14053 + 0.04813$
$= 1.32919$

C_2 : PEI(2) = $3 \times 1.00000 + 0.14053 = 3.14053$

C_3 : PEI(3) = $2 \times 1.00000 + 2 \times 0.14053 = 2.28106$

C_4 : PEI(4) = $1.00000 + 0.14053 + 2 \times 0.04813$
$= 1.23679$

Table 4. Correlation Equations of Linear Change Properties for Alkanes (C_nH_{2n+2}) (Model Equation: $P_{LC(n)} = a + b(n - 1) + c(S_{CNE}) + d(\Delta AOEI) + f(\Delta AIMPI)$)

no	property[a]	range of n[b]	refs	a	b	c	d	f	R[c]	S[c]	N[c]	F[c]
1	V_c	2−28	104	188.34	75.8288	−91.0463	−110.360	−274.627	0.9996	11.71	66	17834.40
2	H_v	2−20	102	0.0000	4.7314	3.04667	9.40258	−13.6059	0.9996	1.39	58	15937.88
3	$\Delta_f H°(g)$	2−18	107	−57.764	−19.759	−5.7347	48.0354	−4.7239	0.9981	3.39	53	3223.22

[a]V_c, critical volume ($cm^3 \cdot mol^{-1}$); H_v, enthalpy of vaporization ($kJ \cdot mol^{-1}$, 29815 K); $\Delta_f H°(g)$, gas enthalpy of formation ($kJ \cdot mol^{-1}$, 29815 K). These properties data are listed in the Supporting Information. [b]Carbon atom number range. [c]R, S, N, and F are correlation coefficient, standard error, number of data points, and Fisher test, respectively.

Table 5. Regression Equations between the Boiling Point, T_b, and Other Nonlinear Change Properties of Noncyclic Alkanes (Model Eqs 26 and 27)

no	property[a]	range of n	a_r (a_s)	b_r (b_s)	c_r (c_s)	d_r (d_s)	f_r (f_s)	R	S	N	F
1	T_c	2−28	0.671645	−0.0002125	−0.12517	0.03554	0.30971	0.9954	0.0091	66	1699.06
2	P_c	2−28	−2.330866	−0.0130645	−1.04390	0.18082	1.50572	0.9982	0.0559	66	4245.89
3	ω[b]	2−36	(−1.332476)	(0.0128386)	(−1.47659)	(−0.28135)	(1.90454)	0.9994	0.0308	93	17927.71
4	C_p	4−16	−1.030352	0.0284990	0.14976	−0.13550	−0.19917	0.9952	0.0119	34	742.55
5	n_D	4−20	−4.561081	−0.0033275	−0.40728	−0.16300	0.02836	0.9963	0.0085	150	4849.88
6	M	5−32	−9.566848	0.0815303	0.87314	−0.70974	−0.06604	0.9922	0.1152	75	1114.16
7	T_F[b]	3−16	(9.191281)	(0.0043236)	(0.92540)	(0.37126)	(−0.06981)	0.9972	0.0211	92	3903.76

[a]Symbols are defined in Table 3, obtained using model eq 26 except when noted otherwise. [b]Obtained using model eq 27.
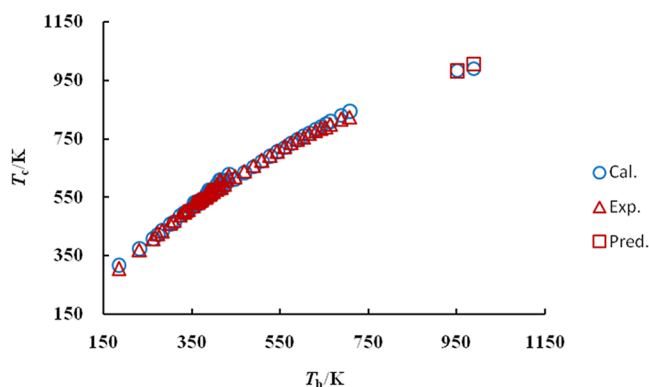
Figure 2. Plot of calculated (○), predicted (□), and experimental (△) critical temperature (T_c) values versus experimental boiling points (T_b) of noncyclic alkanes ($n = 2−100$).

$$C_5 : PEI(5) = 1.00000 + 2 \times 0.14053 + 0.04813$$
$$= 1.32919$$

$$IMPI(b) = \Sigma PEI(i) = 1.32919 + 3.14053 + 2.28106$$
$$+ 1.23679 + 1.32919 = 9.3167$$

$$IMPI(c)$$

$$C_1 : PEI(1) = 1.00000 + 3 \times 0.14053 = 1.42159$$

$$C_2 : PEI(2) = 4 \times 1.00000 = 4.00000$$

$$C_3 : PEI(3) = 1.00000 + 3 \times 0.14053 = 1.42159$$

$$C_4 : PEI(4) = 1.00000 + 3 \times 0.14053 = 1.42159$$

$$C_5 : PEI(5) = 1.00000 + 3 \times 0.14053 = 1.42159$$

$$IMPI(c) = \Sigma PEI(i) = 1.42159 + 4.00000 + 1.42159$$
$$+ 1.42159 + 1.42159 = 9.6863$$

It shows that the IMPI values of *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane are 9.0827, 9.3167, and 9.6863, respectively.

Using abovementioned methods, we calculated the OEI and IMPI values of 149 alkanes bearing 2 to 10 carbon atoms, as shown in Table 2.

2.1.2. Calculation of AOEI, AIMPI, ΔAOEI, and ΔAIMPI of Alkanes. It can be observed from the calculation results in "Section 2.1.1" that the carbon atom numbers of *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane are equal, while the OEI or IMPI values of them are different from each other. Their OEI value order is *n*-pentane (6.8194) > 2-methylbutane (6.4444) > 2,2-dimethylpropane (5.0000), while their IMPI value order is *n*-pentane (9.0827) < 2-methylbutane (9.3167) < 2,2-dimethylpropane (9.5863). Thus, we can employ the differences of OEI and IMPI values between linear and branched alkanes to express the molecular carbon atomic skeleton differences.

Because the OEI and IMPI values are all affected by carbon atoms of alkanes, here we calculate the average values AOEI and AIMPI and employ their differences, ΔAOEI and ΔAIMPI,

Table 6. Regression Equations between the Boiling Point, T_b, and Other Linear Change Properties, V_c, H_v, and $\Delta_f H°(g)$ of Noncyclic Alkanes (Model eq 33)

no	$P(n)$	$P_{LC}(n)$[a]	range of n	a'	b'	c'	d'	f'	g'	R	S	N	F
1	T_b	V_c	2−28	4.737424	0.015400	0.48523	0.21540	−0.02404	−0.000251	0.9995	0.0082	66	12877.90
2	T_b	H_v	2−20	4.708414	−0.001745	0.49456	0.21901	0.00921	0.000049	0.9994	0.0079	58	8570.00
3	T_b	$\Delta_f H°(g)$	2−18	4.808724	0.030819	0.49350	0.15290	0.06966	0.001546	0.9995	0.0060	53	10286.52

[a]Symbols are defined in Table 4.

Table 7. Regression Equations between the Linear Change Properties, V_c, H_v, and $\Delta_f H°(g)$ Against the Boiling Point, T_b, of Noncyclic Alkanes (Model eq 34)

no	$P_{LC(n)}$ [a]	$P_{(n)}$	range of n	a'	b'	c'	d'	f'	g'	R	S	N	F
1	V_c	T_b	2–28	2323.19	74.1747	140.224	0.295647	−254.192	−455.176	0.9996	11.11	66	15845.42
2	H_v	T_b	2–20	0.00000	4.81737	2.15426	9.62160	−12.6000	0.271332	0.9996	1.39	58	12599.01
3	$\Delta_f H°(g)$	T_b	2–18	−1387.84	−19.8372	−142.320	−15.9824	−22.2982	281.830	0.9990	2.57	53	4480.91

[a]Symbols are defined in Table 4.
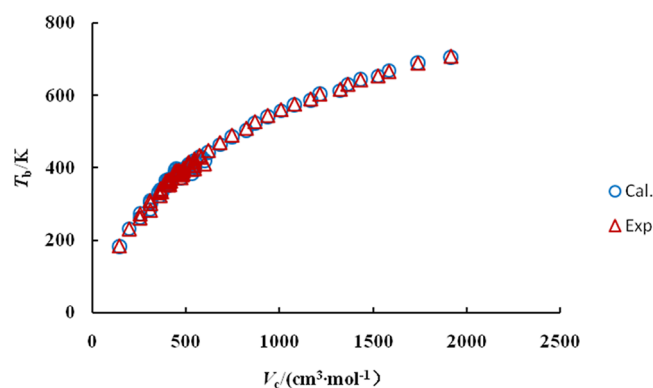
Figure 3. Plot of calculated (○) and experimental (△) boiling point (T_b) values versus the critical volume (V_c) of noncyclic alkanes ($n = 2–28$).
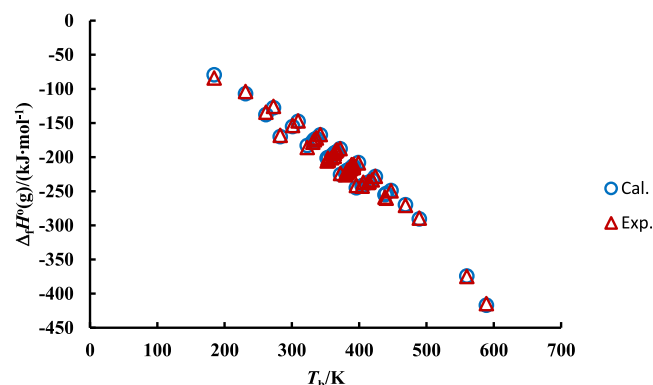
Figure 4. Plot of calculated (○) and experimental (△) values of gas enthalpies of formation $[\Delta_f H°(g)]$ versus experimental boiling points (T_b) of noncyclic alkanes ($n = 2–18$).

between linear and branched alkanes to express the molecular carbon atomic skeleton differences, that is

$$AOEI = OEI / n \tag{18}$$

$$AIMPI = IMPI / n \tag{19}$$

$$\Delta AOEI = AOEI_{br} − AOEI_{lin} \tag{20}$$

$$\Delta AIMPI = AIMPI_{br} − AIMPI_{lin} \tag{21}$$

In eqs 18−21, the n is the carbon atom number in the alkane molecule, the subscript br and lin represent branched alkane and linear alkane, which have an equal carbon atom number, respectively. Equations 20 and 21 mean that the $\Delta AOEI$ and $\Delta AIMPI$ values of linear alkanes all are zero.

Take the calculations of AOEI and AIMPI of Figure 1a−c for examples. The three molecules all have five carbon atoms ($n = 5$), thus, their AOEI and AIMPI are calculated as follows

Calculation of AOEI

$$AOEI(a) = OEI(a) / n = 6.8194 / 5 = 1.3639$$

$$AOEI(b) = OEI(b) / n = 6.4444 / 5 = 1.2889$$

$$AOEI(c) = OEI(c) / n = 5.0000 / 5 = 1.0000$$

Calculation of AIMPI

$$AIMPI(a) = IMPI(a) / n = 9.0827 / 5 = 1.8165$$

$$AIMPI(b) = IMPI(b) / n = 9.3167 / 5 = 1.8633$$

Table 8. Estimation Accuracy for the Properties of Noncyclic Alkanes by Using the Obtained Model Equations in Tables 3 and 4, and Estimation Results of Other Works

property[a]	range of n[b]	N[c]	this work RMSE[d]	AAE[d]	AAPE %[d]	other works RMSE[d]	AAE[d]	AAPE %[d]	refs
T_b	2−100	210	3.96	2.97	0.67	7.9	6.17	1.44	37
T_c	2−28	66	5.07	3.47	0.60	10.77	7.72	1.23	37
P_c	2−28	66	0.060	0.037	1.63	2.38	1.4	2.228, 3.90	18, 37
ω	2−36	93	0.012	0.0080	1.81	0.1002	0.0534, 0.0130	11.09, 4.08	37, 55
D	5−17	61	0.0132	0.0065	0.87	0.0185			102
C_p	4−16	34	2.30	1.70	0.71	3.5		3, 2.682	17, 18, 64
n_D	4−20	150	0.0060	0.0027	0.19	0.0136			102
P_v[e]	2−16	63	0.121	0.074	2.01			3.4, 9.8	53, 88
Ip	2−11	20	0.031	0.024	0.24	0.1193			105
S_w[e]	2−10	24	0.011	0.084	2.02	0.167			105
μ	5−35	78	0.264	0.1978	9.51		0.21		106
T_F	3−16	92	4.52	3.51	1.26	12.01, 5.58	8.97	2.8	37, 93
V_c	2−28	66	11.42	8.93	1.87	11.65	7.97	1.915, 2.05	18, 37
H_v	2−20	58	1.36	0.88	3.19	1.42, 1.9	0.95	2.66, 4.08	37, 46, 77
$\Delta_f H°(g)$	2−18	53	3.29	2.59	1.24	7.04, 6.74	5.03		37, 68

[a]Symbols are defined in Tables 3 and 4. [b]Carbon atom number range. [c]Number of data points. [d]Symbols RMSE, AAE, and AAPE represent root mean square error, AAE, and AAPE, respectively. The AAE and AAPE of ω in ref 55 include alkanes and cycloalkanes. In this work, the RMSE is obtained from the calculated and experimental values. [e]The regression of P_v is in the form of log P_v; the regression of S_w is in the form of −log S_w.

$$AIMPI(c) = IMPI(c) / n = 9.6863 / 5 = 1.9372$$

Calculation of ΔAOEI:

It is known that AOEI value of n-pentane is AOEI(a) = 1.3639; therefore

$$\Delta AOEI(a) = AOEI(a) − AOEI(a) = 1.3639 − 1.3639$$
$$= 0.0000$$

$$\Delta AOEI(b) = AOEI(b) − AOEI(a) = 1.2889 − 1.3639$$
$$= −0.0750$$

$$\Delta AOEI(c) = AOEI(c) − AOEI(a) = 1.0000 − 1.3639$$
$$= −0.3639$$

The calculation results show that the ΔAOEI values of n-pentane, 2-methylbutane, and 2,2-dimethylpropane are 0.0000, −0.0750, and −0.3639, respectively.

Calculation of ΔAIMPI:

It is known that AIMPI value of n-pentane is AIMPI(a) = 1.8165; therefore

$$\Delta AIMPI(a) = AIMPI(a) − AIMPI(a) = 1.8165 − 1.8165$$
$$= 0.0000$$

$$\Delta AIMPI(b) = AIMPI(b) − AIMPI(a) = 1.8633 − 1.8165$$
$$= 0.0468$$

$$\Delta AIMPI(c) = AIMPI(c) − AIMPI(a) = 1.9372 − 1.8165$$
$$= 0.1207$$

The calculation results show that the ΔAIMPI values of n-pentane, 2-methylbutane, and 2,2-dimethylpropane are 0.0000, 0.0468, and 0.1207, respectively.

In this study, the parameters both ΔAOEI and ΔAIMPI are used to express molecular structure difference between linear and branched alkane isomers.

2.1.3. General Equation Expressing the Properties of Noncyclic Alkanes. In our previous paper,[101] the NPOH

equation was proposed to express changes in the physicochemical properties of organic homologues, as shown eq 22

$$\ln(P_{(n)}) = a + b(n − 1) + c(S_{CNE}) \tag{22}$$

where $P_{(n)}$ represents property of linear alkane H−(CH$_2$)$_n$−H, n is repeating structural unit (CH$_2$) number, and S_{CNE} is "sum of carbon number effects," the term $\sum_{i=2}^n \left(\frac{1}{i-1}\right)$.

For the isomers of linear alkanes, they have an equal carbon atom number in the molecular structure. Their properties should be dominated by the carbon atom number n and the characteristic parameters of molecular structure. If the former is denoted by $(n − 1)$ and S_{CNE}, the latter is denoted by ΔAOEI and ΔAIMPI, then we can establish a general equation, *via* taking the parent linear alkane molecule as reference and adding parameters ΔAOEI and ΔAIMPI into eq 22, to express the properties of noncyclic alkanes (involving linear and branched alkane isomers), as shown in eq 23

$$\ln(P_{(n)}) = a + b(n − 1) + c(S_{CNE}) + d(\Delta AOEI)$$
$$+ f(\Delta AIMPI) \tag{23}$$

It should be noted that, in eq 23, the ΔAOEI and ΔAIMPI values all are zero for the linear alkane molecules; in such cases, eq 23 will return to eq 22. For convenience, eq 23 is named the "NPNA equation" (i.e., the abbreviation of "nonlinear properties of noncyclic alkanes equation").

2.2. Applicability of NPNA Equation. *2.2.1. Correlation with the Properties of Alkanes.* In order to test the applicability of NPNA eq 23, quantitative correlation analysis was conducted using various physicochemical properties (nonlinear changes) of noncyclic alkanes. First, the ΔAOEI and ΔAIMPI values were calculated with the methods described in "Sections 2.1.1 and 2.1.2," and the S_{CNE} values were directly taken from our earlier paper.[101] Then, using eq 23 as a model equation, we performed regression analysis of properties $P_{(n)}$ of noncyclic alkanes. The results are shown in Table 3.

It can be observed, from the results of Table 3, that most of the correlation coefficients (R) (except for D and n_D properties)
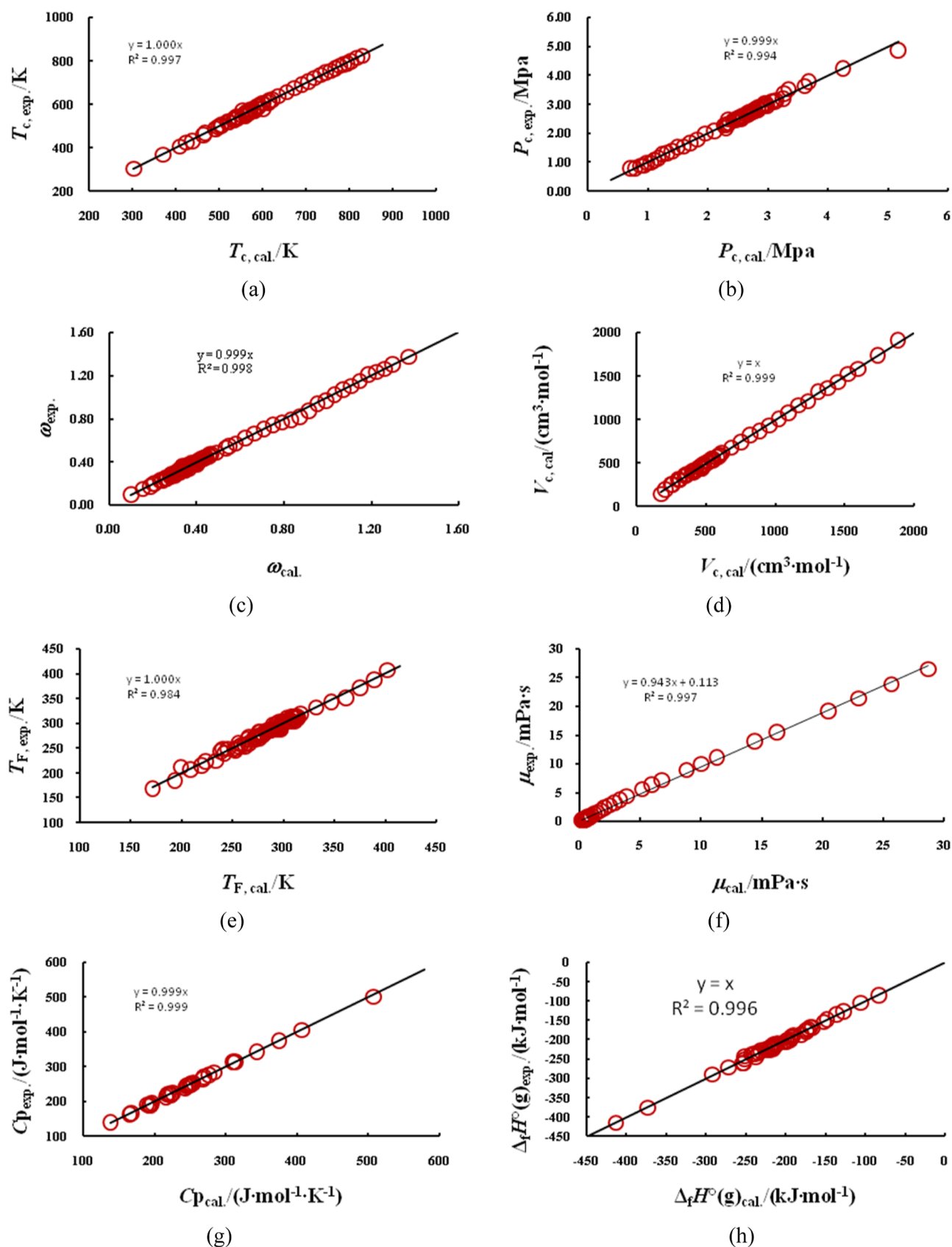
Figure 5. Plot of calculated versus experimental (a) T_c, (b) P_c, (c) ω, (d) V_c, (e) T_F, (f) μ, (g) C_p, and (h) $\Delta_f H°(g)$ values of noncyclic alkanes.

were above 0.99 for the various properties of noncyclic alkanes, indicating that eq 23 can be used to express the regularity of property changes of noncyclic alkanes. In Table 3, the

correlation coefficients R are 0.9315 and 0.9414 for D (no. 5) and n_D (no. 7), respectively. Since the data distribution ranges of D (liquid density, $g \cdot cm^{-3}$) and n_D (refractive index) are narrow,

in 0.6201−0.8242 and 1.3326−1.4695, respectively, the correlation coefficients of the equations are less than 0.99. Indeed, in Yuan's report,[99] the correlation coefficients of correlation equations involving properties D and n_D are also less than those of other properties. However, the calculation accuracy of eqs 5 and 7 are satisfactory, in which, the average absolute percentage error (AAPE) of density (D) is only 0.87% for 61 compounds used in the equation and that of refractive index (n_D) is only 0.19% for 150 compounds used in the equation. Properties with different change regularities for noncyclic alkanes which can have the same expression is surprising and have not been reported previously.

In our previous paper,[101] eq 24 was suggested to express the linear change property, $P_{LC(n)}$, of homologues. Thus, in this work, we try to add parameters ΔAOEI and ΔAIMPI into eq 24 for expressing the linear change property of noncyclic alkanes, as shown in eq 25:

$$P_{LC(n)} = a + b(n-1) + c(S_{CNE}) \tag{24}$$

$$P_{LC(n)} = a + b(n-1) + c(S_{CNE}) + d(\Delta AOEI) \\ + f(\Delta AIMPI) \tag{25}$$

Take the critical volume (V_c), enthalpies of vaporization (H_v), and gas enthalpies of formation [$\Delta_f H°(g)$], for example, we employed eq 25 as a model equation to perform regression analysis of properties, V_c, H_v, and $\Delta_f H°(g)$, of noncyclic alkanes. The obtained regression equations are listed in Table 4.

The correlation coefficients (R) of correlation equations in Table 4 are all above 0.99, indicating that eq 25 is suitable for expressing the linear change properties of noncyclic alkanes. Of course, for some linear change properties of noncyclic alkanes, such as molar mass (M_{mol}), coefficients c, d, and f in eq 25 all are equal to zero, meaning that terms S_{CNE}, ΔAOEI, and ΔAIMPI do not need to be employed in such cases.

2.2.2. Relationship between Properties of Alkanes. Equations 23 and 25 show that both linear and nonlinear change properties of noncyclic alkanes can be correlated with the parameters n, S_{CNE}, ΔAOEI, and ΔAIMPI, which implies that we can link the change regularities of different properties of noncyclic alkanes *via* using the parameters n, S_{CNE}, ΔAOEI, and ΔAIMPI.

2.2.2.1. Relationship between Nonlinear Change Properties. If one property of noncyclic alkanes is $P_{(n)}$ (such as boiling point) and the other property is $P'_{(n)}$ (such as critical temperature), from eq 23, we can theoretically obtain eqs 26 and 27:

$$[\ln(P_{(n)}) - \ln(P'_{(n)})] = (a - a') + (b - b')(n-1) \\ + (c - c')(S_{CNE}) + (d - d')(\Delta AOEI) \\ + (f - f')(\Delta AIMPI)$$

$$= a_r + b_r(n-1) + c_r(S_{CNE}) + d_r(\Delta AOEI) \\ + f_r(\Delta AIMPI) \tag{26}$$

$$[\ln(P_{(n)}) + \ln(P'_{(n)})] = (a + a') + (b + b')(n-1) \\ + (c + c')(S_{CNE}) + (d + d')(\Delta AOEI) \\ + (f + f')(\Delta AIMPI)$$

$$= a_s + b_s(n-1) + c_s(S_{CNE}) + d_s(\Delta AOEI) \\ + f_s(\Delta AIMPI) \tag{27}$$

In eq 26, $a_r = a - a'$, $b_r = b - b'$, $c_r = c - c'$, $d_r = d - d'$ and $f_r = f - f'$, while in eq 27, $a_s = a + a'$, $b_s = b + b'$, $c_s = c + c'$, $d_s = d + d'$, and $f_s = f + f'$. For the two specific physicochemical properties, $P_{(n)}$ and $P'_{(n)}$, of noncyclic alkanes, parameters a_r, b_r, c_r, d_r, f_r, a_s, b_s, c_s, d_s, and f_s can be obtained using the regression method.

When the logarithms of eqs 26 and 27 are removed, they can be expressed as eqs 28 and 29:

$$P_{(n)} = P'_{(n)} e^{a_r}(e^{b_r})^{(n-1)} e^{c_r S_{CNE}} e^{d_r(\Delta AOEI)} e^{f_r(\Delta AIMPI)} \tag{28}$$

$$P_{(n)} = [P'_{(n)}]^{-1} e^{a_s}(e^{b_s})^{(n-1)} e^{c_s S_{CNE}} e^{d_s(\Delta AOEI)} e^{f_s(\Delta AIMPI)} \tag{29}$$

Equations 26 and 27 (or eqs 28 and 29) are the relationship between two properties of noncyclic alkanes. By using eqs 26 and 27 (or eqs 28 and 29), one property of noncyclic alkanes can be correlated with another property, providing simple and convenient correlation of the noncyclic alkane properties.

Take T_c and T_b of noncyclic alkanes, for example, we used eq 26 as a model equation and obtained the relationship between T_c and T_b, as shown in eq 30 (also no. 1 of Table 5), in which the alkanes used is same as the no. 2 in Table 3.

$$T_{c(n)} = T_{b(n)} \times 1.957455 \times 0.999788^{(n-1)} \times e^{-0.12517 S_{CNE}} \\ e^{0.035541(\Delta AOEI)} e^{0.309706(\Delta AIMPI)}$$

$$= T_{b(n)} \times 1.957455 \times 0.999788^{(n-1)} \\ \times e^{(-0.12517 S_{CNE} + 0.035541(\Delta AOEI) + 0.309706(\Delta AIMPI))}$$

$$R = 0.9954, S = 0.0091, N = 66, F = 1699.06 \tag{30}$$

Equation 30 is the quantitative relationship between T_b and T_c for noncyclic alkanes. Using eq 30, T_c of noncyclic alkanes can be calculated from their T_b. The calculated results show that the average absolute error (AAE) between the experimental value ($T_{c\ exp.}$) and calculated value ($T_{c\ cal.}$) was 3.40 K, and the AAPE was 0.58% for the 66 alkanes ($n = 2-28$). The plot of the calculated, predicted by Bychinsky[38] (n-C_{80} and n-C_{100}), and experimental values of critical temperature versus the boiling point of noncyclic alkanes is as shown in Figure 2.

As further examples, eqs 26 and 27 were used as model equations to quantitatively correlate the boiling points of noncyclic alkanes with other properties, P_c, ω, C_p, n_D, μ, and T_F. The results are listed in Table 5, which shows that any nonlinear change property of noncyclic alkanes can be correlated with the boiling point.

2.2.2.2. Relationship between Nonlinear and Linear Change Properties of Noncyclic Alkanes. Equations 23 and 25 express the change regularities of the nonlinear and linear change properties of noncyclic alkanes, respectively, notably they have the same variables, $(n − 1)$, S_{CNE}, ΔAOEI, and ΔAIMPI. Therefore, we can establish a correlation between the nonlinear and linear change properties of noncyclic alkanes by combining eqs 23 and 25, as shown in eqs 31 and 32

$$\ln(P_{(n)}) - P_{LC(n)} = a' + b'(n-1) + c'(S_{CNE}) + d'(\Delta AOEI) \\ + f'(\Delta AIMPI) \tag{31}$$

or

$$P_{LC(n)} - \ln(P_{(n)}) = a' + b'(n-1) + c'(S_{CNE}) + d'(\Delta AOEI) \\ + f'(\Delta AIMPI) \tag{32}$$

Equations 31 and 32 can also be written as eqs 33 and 34

$$\ln(P_{(n)}) = a' + b'(n-1) + c'(S_{CNE}) + d'(\Delta AOEI)$$
$$+ f'(\Delta AIMPI) + g' P_{LC(n)} \tag{33}$$

$$P_{LC(n)} = a' + b'(n-1) + c'(S_{CNE}) + d'(\Delta AOEI)$$
$$+ f'(\Delta AIMPI) + g' \ln(P_{(n)}) \tag{34}$$

where for the two specific physicochemical properties, $P_{(n)}$ and $P_{LC(n)}$, of noncyclic alkanes, parameters a', b', c', d', f', and g' can be obtained by using the regression method.

Using the critical volume (V_c), enthalpies of vaporization (H_v), and gas enthalpies of formation ($\Delta_f H°(g)$) of noncyclic alkanes as examples, the correlation equations between the boiling point (T_b) and V_c, H_v and $\Delta_f H°(g)$ were obtained, *via* employing eq 33 as a model equation and using the regression method, as shown in Table 6. When we used eq 34 as a model equation to carry out regression, we got the regression equations listed in Table 7.

The results in Tables 5 and 7 show that the correlation between the nonlinear and linear change properties of noncyclic alkanes can be established well by employing model eqs 33 or 34, that is, one nonlinear change property could be estimated by using another linear change property of noncyclic alkanes, and vice versa. The following are two calculation examples.

Example 1

Using equation 1 in Table 6, the boiling point (T_b) of noncyclic alkanes can be calculated from their critical volume (V_c). The AAE between the experimental value ($T_{b\ exp.}$) and calculated value ($T_{b\ cal.}$) was 2.48 K, and the AAPE was 0.61% for the 66 compounds ($n = 2-28$) used in the equation. Figure 3 shows the plot of the calculated and experimental values of boiling point versus the critical volume of noncyclic alkanes.

Example 2:

Using equation 3 in Table 7, the gas enthalpies of formation, $\Delta_f H°(g)$, of noncyclic alkanes can be calculated from their boiling point (T_b). The AAE between the experimental value $[\Delta_f H°(g)_{exp.}]$ and calculated value $[\Delta_f H°(g)_{cal.}]$ was 1.91 kJ·mol^{-1} (exhibiting chemical accuracy, i.e., a maximum 4.2 kJ·mol^{-1} difference[70]), and the AAPE was 1.01% for the 53 compounds ($n = 2-18$) used in equation. Figure 4 shows a plot of the calculated and experimental values of gas enthalpy of formation versus the boiling points of noncyclic alkanes.

The above results show that any two properties of noncyclic alkanes can be correlated with four parameters, n, S_{CNE}, $\Delta AOEI$, and $\Delta AIMPI$, without complex equations.

2.2.3. Prediction of Properties of Alkanes. Using the model equations in Tables 3 and 4, we can predict the properties of alkanes. First, we check up the estimation accuracy of these model equations *via* employing the model equations in Tables 3 and 4 to calculate the properties of alkanes and comparing the calculated values against the experimental values. The obtained results are listed in Table 8, showing good estimation accuracy, and the AAPE % of all properties (except for μ property) of alkanes are less than 3.5%. Some examples of calculated versus experimental values are as shown in Figure 5, indicating the calculated values are in good agreement with the experimental values.

Here, we also compared the estimation results of this work with those of other works. It should be noted that it is difficult to compare the results reported in different works because the data sets and number of variables employed in the various works were different. Particularly, many of the other works only involve

alkanes with less than 11 carbon atoms. Nevertheless, some comparisons as follows are instructive. Allison et al.,[108] in 2022, obtained AAE 6 K (corresponding to AAPE 1.32%) by using a graph convolutional neural network to predict of normal boiling point. In this work, some estimation results reported in other works were also collected in Table 8.

It can be observed, from Table 8, that the RMSE, AAE, or AAPE % values of this work are less than those of other works for each property of noncyclic alkanes, indicating that the equations in Tables 3 and 4 are reliable. In addition, the methods of this work also has the advantages of uniform expression and usage of fewer parameters. Thus, we can use the equations in Tables 3 and 4 to predict the corresponding properties of noncyclic alkanes. In this work, we predicted some properties of noncyclic alkanes involving carbon atom numbers 2−40 and all isomers with carbon atoms 2−10 and listed them in Table S2 of the Supporting Information. These predicted property data are 142 critical temperatures, 142 critical pressures, 115 acentric factors, 116 flash points, 174 heat capacities, 142 critical volumes, and 155 gas enthalpies of formation, total of 986 values, which has not be experimentally measured.

The predicted properties of this work can also be applied in other fields. For example, the predicted $\Delta_f H°(g)$ values can be used for optimizing combustion processes of fuels. It is known that the relationship between enthalpy of combustion $\Delta_c H°(g)$ (kJ·mol^{-1}) at 298.15 K and $\Delta_f H°(g)$ of alkanes ($C_n H_{2n+2}$) can be expressed by eq 35[104]

$$\Delta_c H°(g) / (kJ·mol^{-1}) = 393.51n + 142.915(2n + 2)$$
$$+ \Delta_f H°(g) / (kJ·mol^{-1}) \tag{35}$$

Thus, using eq 35 and the $\Delta_f H°(g)$ of alkanes, we can calculate their $\Delta_c H°(g)$. Take $C_9 H_{20}$ as an example, the predicted $\Delta_f H°(g)$ values of *n*-nonane and 2,2,4-trimethylhexane are −231.4 and −242.7 kJ·mol^{-1}, respectively. Their calculated $\Delta_c H°(g)$ values are 6168.47 (experimental value 6170.98)[80] and 6157.21 (no experimental value). The calculated results show that the linear isomer has more enthalpy of combustion than branched isomers.

3. CONCLUSIONS

The research result of this work shows that based on the NPOH equation,[101] a general NPNA equation (equation 23) can be obtained *via* adding structural parameters $\Delta AOEI$ and $\Delta AIMPI$ that characterize the molecular carbon atomic skeleton difference between linear and branched alkane isomers. The various nonlinear change properties of noncyclic alkanes can be expressed by using NPNA equation, while for the various linear change properties of noncyclic alkanes, they can be expressed by using general eq 25. Therefore, both nonlinear and linear change properties of noncyclic alkanes can be correlated with four parameters, the number of carbon atoms (n), the "sum of carbon number effects" (S_{CNE}), average odd-even index difference ($\Delta AOEI$), and average inner molecular polarizability index difference ($\Delta AIMPI$). Furthermore, using the four parameters n, S_{CNE}, $\Delta AOEI$, and $\Delta AIMPI$, a quantitative correlation equation can be established between any two properties of noncyclic alkanes.

This work extended the NPOH equation and provided a simple and convenient estimation or prediction method for the properties of noncyclic alkanes. It can be widely used in studying QSPRs of noncyclic alkanes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c06856.

Physicochemical properties of alkanes and the predicted values of some properties of noncyclic alkanes (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Chenzhong Cao — *Key Laboratory of Theoretical Organic Chemistry and Function Molecule, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China;* ⓞ orcid.org/0000-0001-5224-7716; Email: czcao@hnust.edu.cn

Author

Chao-Tun Cao — *Key Laboratory of Theoretical Organic Chemistry and Function Molecule, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China;* ⓞ orcid.org/0000-0002-3390-7587

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c06856

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Baled, H. O.; Gamwo, I. K.; Enick, R. M.; McHugh, M. A. M. A. Viscosity models for pure hydrocarbons at extreme conditions: A review and comparative study. *Fuel* **2018**, *218*, 89−111.

(2) Macías-Salinas, R. Modeling the thermal conductivity of n-alkanes via the use of density scaling. *J. Chem. Thermodyn.* **2018**, *116*, 363−371.

(3) Farzi, N.; Rezaei, M. Modeling of n-alkanes and refrigerants with a hard convex body chain equation of state. *Int. J. Refrig.* **2018**, *86*, 139−153.

(4) He, M.; Wang, C.; Chen, J.; Liu, X. Prediction of the critical properties of mixtures based on group contribution theory. *J. Mol. Liq.* **2018**, *271*, 313−318.

(5) Liu, Y.; He, X.; Zhao, X.; Wang, X.; Zheng, X. Modeling heat capacity of saturated hydrocarbon in liquid phase over a wide range of temperature and pressure. *J. Mol. Liq.* **2020**, *319*, 114068.

(6) Le Neindre, B.; Lombardi, G.; Desmarest, P.; Kayser, M.; Sabirzianov, A. N.; Gabitov, F. R.; Gumerov, F.; Garrabos, Y. Thermal conductivity of gaseous and liquid n-hexane. *Fluid Phase Equilib.* **2018**, *474*, 60−75.

(7) Tassin, N. G.; Mascietti, V. A.; Cismondi, M. Phase behavior of multicomponent alkane mixtures and evaluation of predictive capacity for the PR and RKPR EoS's. *Fluid Phase Equilib.* **2019**, *480*, 53−65.

(8) Lv, Y.; Tian, J.; Jiang, H. Three-parameter correlation for the temperature dependent thermal conductivity of saturated liquids. *Fluid Phase Equilib.* **2020**, *514*, 112563.

(9) Ramana, A. S. V.; Elliott, J. R. A complete integral equation theory for accurate thermodynamics of chain molecules. *Fluid Phase Equilib.* **2019**, *494*, 21−32.

(10) Zheng, X.; Qu, D.; Zhang, F.; Liu, Y.; Qin, G. Measurements and calculations of thermal conductivity for liquid n-octane and n-decane. *Fluid Phase Equilib.* **2021**, *533*, 112940.

(11) Kundu, G.; Kumar, A. Optimized critical parameters for n-alkanes up to C100 for reliable multiphase behavior of hydrocarbon mixture using SRK EOS. *Fluid Phase Equilib.* **2021**, *541*, 113037.

(12) Peng, H.; Zhang, D.; Ling, X.; Li, Y.; Wang, Y.; Yu, Q.; She, X.; Li, Y.; Ding, Y. n-Alkanes Phase Change Materials and Their Micro-encapsulation for Thermal Energy Storage: A Critical Review. *Energy Fuels* **2018**, *32*, 7262−7293.

(13) Vinhal, A. P. C. M.; Yan, W.; Kontogeorgis, G. M. Modeling the Critical and Phase Equilibrium Properties of Pure Fluids and Mixtures with the Crossover Cubic-Plus-Association Equation of State. *J. Chem. Eng. Data* **2020**, *65*, 1095−1107.

(14) Portnova, S. V.; Yamshchikova, Y. F.; Krasnykh, E. L.; Nikitin, E. D.; Popov, A. P.; Faizullin, M. Z. Vapor Pressure, Vaporization Enthalpies, Critical Parameters, and Heat Capacities of Alkyl Glycolates. *J. Chem. Eng. Data* **2020**, *65*, 2566−2577.

(15) Gong, Z.; Wu, Y.; Wu, L.; Sun, H. Predicting Thermodynamic Properties of Alkanes by High-Throughput Force Field Simulation and Machine Learning. *J. Chem. Inf. Model.* **2018**, *58*, 2502−2516.

(16) Hekayati, J.; Raeissi, S. Estimation of the critical properties of compounds using volume-based thermodynamics. *AIChE J.* **2020**, *66*, No. e17004.

(17) Bloxham, J. C.; Giles, N. F.; Knotts, T. A.; Wilding, W. V. A Liquid Heat Capacity Limit for Organic Compounds. *Int. J. Thermophys.* **2022**, *43*, 96.

(18) Csemány, D.; Gujás, I.; Chong, C. T.; Józsa, V. Evaluation of material property estimating methods for n-alkanes, 1-alcohols, and methyl esters for droplet evaporation calculations. *Heat Mass Transfer* **2021**, *57*, 1965−1979.

(19) Ambrose, D.; Tsonopoulos, C. Vapor-Liquid Critical Properties of Elements and Compounds. 2. Normal Alkanes. *J. Chem. Eng. Data* **1995**, *40*, 531−546.

(20) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure, Heat Capacity, and Density along the Saturation Line: Measurements for Benzenamine, Butylbenzene, sec-Butylbenzene, tert-Butylbenzene, 2,2-Dimethylbutanoic Acid, Tridecafluoroheptanoic Acid, 2-Butyl-2-ethyl-1,3-propanediol, 2,2,4-Trimethyl-1,3-pentane-diol, and 1-Chloro-2-propanol. *J. Chem. Eng. Data* **2002**, *47*, 648−666.

(21) Lemmon, E. W.; McLinden, M. O.; Wagner, W. Thermodynamic Properties of Propane. III. A Reference Equation of State for Temperatures from the Melting Line to 650 K and Pressures up to 1000 MPa. *J. Chem. Eng. Data* **2009**, *54*, 3141−3180.

(22) Cibulka, I.; Hnědkovský, L. Liquid Densities at Elevated Pressures of n-Alkanes from C_5 to C_{16}: A Critical Evaluation of Experimental Data. *J. Chem. Eng. Data* **1996**, *41*, 657−668.

(23) Daubert, T. E. Vapor−Liquid Critical Properties of Elements and Compounds. 5. Branched Alkanes and Cycloalkanes. *J. Chem. Eng. Data* **1996**, *41*, 365−372.

(24) Nichols, T. T.; Utgikar, V. P. Wagner Equation Predicting Entire Curve for Pure Fluids from Limited VLE Data: Critical and Normal Boiling Points & Acentric Factor. *Int. J. Thermodyn.* **2018**, *21*, 158−172.

(25) Grigoriev, B.; Alexandrov, I.; Gerasimov, A. Application of multiparameter fundamental equations of state to predict the thermodynamic properties and phase equilibria of technological oil fractions. *Fuel* **2018**, *215*, 80−89.

(26) Kumar, A.; Upadhyay, R. A new two-parameters cubic equation of state with benefits of three-parameters. *Chem. Eng. Sci.* **2021**, *229*, 116045.

(27) Saiteja, P.; Ashok, B. A critical insight review on homogeneous charge compression ignition engine characteristics powered by biofuels. *Fuel* **2021**, *285*, 119202.

(28) Mukherjee, P. K. Phase transitions among the rotator phases of the normal alkanes: A review. *Phys. Rep.* **2015**, *588*, 1−54.

(29) Le Neindre, B.; Lombardi, G.; Desmarest, P.; Kayser, M.; Sabirzianov, A. N.; Gabitov, F. R.; Gumerov, F.; Garrabos, Y. Thermal conductivity of gaseous and liquid n-hexane. *Fluid Phase Equilib.* **2018**, *474*, 60.

(30) Zhao, W.; Shanmukha, M. C.; Usha, A.; Farahani, M. R.; Shilpa, K. C. Computing SS Index of Certain Dendrimers. *J. Math.* **2021**, *2021*, 7483508.

(31) Mulero, A.; Cachadiña, I.; Cardona, L. F.; Valderrama, J. O. Pressure-Surface Tension-Temperature Equation of State for n-Alkanes. *Ind. Eng. Chem. Res.* **2022**, *61*, 3457−3473.

(32) Taherzadeh, M.; Haghbakhsh, R.; Duarte, A. R. C.; Raeissi, S. Generalized Model to Estimate the Refractive Indices of Deep Eutectic Solvents. *J. Chem. Eng. Data* **2020**, *65*, 3965−3976.

(33) Xing, H.; Chen, J.; Zhang, Y.; Chen, L.; He, M.; Zhang, Y. Measurement of Thermal Diffusivity of n-Pentane from (293-573) K and up to 10.0 MPa in the Near-Critical and Supercritical Regions. *J. Chem. Eng. Data* **2021**, *66*, 4697−4705.

(34) Vinhal, A. P. C. M.; Yan, W.; Kontogeorgis, G. M. Application of a Crossover Equation of State to Describe Phase Equilibrium and Critical Properties of n-Alkanes and Methane/n-Alkane Mixtures. *J. Chem. Eng. Data* **2018**, *63*, 981−993.

(35) Barsotti, E.; Tan, S. P.; Piri, M.; Chen, J.-H. Phenomenological Study of Confined Criticality: Insights from the Capillary Condensation of Propane, n-Butane, and n-Pentane in Nanopores. *Langmuir* **2018**, *34*, 4473−4483.

(36) Cachadiña, I.; Mulero, A. Evaluation of correlations for prediction of the normal boiling enthalpy. *Fluid Phase Equilib.* **2006**, *240*, 173−178.

(37) Hukkerikar, A. S.; Sarup, B.; Ten Kate, A. T.; Abildskov, J.; Sin, G.; Gani, R. Group-contribution+ (GC+) based estimation of properties of pure components: Improved property estimation and uncertainty analysis. *Fluid Phase Equilib.* **2012**, *321*, 25−43.

(38) Bychinsky, V. A.; Tupitsyn, A. A.; Chudnenko, K. V.; Mukhetdinova, A. V. Methods for Calculating the Critical Constants of Hydrocarbons (Using the n-Alkane Series as an Example). *J. Chem. Eng. Data* **2013**, *58*, 3102−3109.

(39) Hemmati-Sarapardeh, A.; Ameli, F.; Varamesh, A.; Shamshirband, S.; Mohammadi, A. H.; Dabir, B. Toward generalized models for estimating molecular weights and acentric factors of pure chemical compounds. *Int. J. Hydrogen Energy* **2018**, *43*, 2699−2717.

(40) Khoshsima, A.; Hosseini, A. Prediction of the Boyle temperature, second virial coefficient and Zeno line using the cubic and volume - translated cubic equations of state. *J. Mol. Liq.* **2017**, *242*, 625−639.

(41) Lopes, J. T.; Franco, L. F. M. A possible way to explicitly account for different molecular geometries with an equation of state. *J. Mol. Liq.* **2021**, *330*, 115676.

(42) Lashkarbolooki, M.; Hezave, A. Z.; Bayat, M. Correlating thermal conductivity of pure hydrocarbons and aromatics via perceptron artificial neural network (PANN) method. *Int. J. Hydrogen Energy* **2017**, *25*, 547−554.

(43) Penfold, R.; Abbas, S.; Nordholm, S. Effective potential approach to bulk thermodynamic properties and surface tension of molecular fluids I. Single component n-alkane systems. *Fluid Phase Equilib.* **1996**, *120*, 39−67.

(44) Homer, J.; Generalis, S. C.; Robson, J. H. Artificial neural networks for the prediction of liquid viscosity, density, heat of vaporization, boiling point and Pitzer's acentric factor Part I. Hydrocarbons. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4075−4081.

(45) Mersmann, A.; Kind, M. Prediction of Mechanical and Thermal Properties of Pure Liquids, of Critical Data, and of Vapor Pressure. *Ind. Eng. Chem. Res.* **2017**, *56*, 1633−1645.

(46) Chen, Z.; Yang, D. Optimization of the Reduced Temperature Associated with Peng-Robinson Equation of State and Soave-Redlich-Kwong Equation of State To Improve Vapor Pressure Prediction for Heavy Hydrocarbon Compounds. *J. Chem. Eng. Data* **2017**, *62*, 3488−3500.

(47) Li, H.; Yang, D. Modified α Function for the Peng−Robinson Equation of State To Improve the Vapor Pressure Prediction of Non-hydrocarbon and Hydrocarbon Compounds. *Energy Fuels* **2011**, *25*, 215−223.

(48) Mehrotra, A. K. Generalized One-Parameter Viscosity Equation for Light and Medium Liquid Hydrocarbons. *Ind. Eng. Chem. Res.* **1991**, *30*, 1367−1372.

(49) Mejía, A.; Herdes, C.; Müller, E. A. Force Fields for Coarse-Grained Molecular Simulations from a Corresponding States Correlation. *Ind. Eng. Chem. Res.* **2014**, *53*, 4131−4141.

(50) Kontogeorgis, G. M.; Smirlis, I.; Yakoumis, I. V.; Harismiadis, V.; Tassios, D. P. Method for Estimating Critical Properties of Heavy Compounds Suitable for Cubic Equations of State and Its Application to the Prediction of Vapor Pressures. *Ind. Eng. Chem. Res.* **1997**, *36*, 4008−4012.

(51) Gamba, S.; Soave, G. S.; Pellegrini, L. A. Use of normal boiling point correlations for predicting critical parameters of paraffins for vapour-liquid equilibrium calculations with the SRK equation of state. *Fluid Phase Equilib.* **2009**, *276*, 133−141.

(52) Marano, J. J.; Holder, G. D. General Equation for Correlating the Thermophysical Properties of n-Paraffins, n-Olefins, and Other Homologous Series. 1. Formalism for Developing Asymptotic Behavior Correlations. *Ind. Eng. Chem. Res.* **1997**, *36*, 1887−1894.

(53) Kumar, A.; Okuno, R. Critical parameters optimized for accurate phase behavior modeling for heavy n-alkanes up to C100 using the Peng-Robinson equation of state. *Fluid Phase Equilib.* **2012**, *335*, 46−59.

(54) Gharagheizi, F.; Eslamimanesh, A.; Mohammadi, A. H.; Richon, D. Determination of Critical Properties and Acentric Factors of Pure Compounds Using the Artificial Neural Network Group Contribution Algorithm. *J. Chem. Eng. Data* **2011**, *56*, 2460−2476.

(55) Wang, Q.; Jia, Q.; Ma, P. Prediction of the Acentric Factor of Organic Compounds with the Positional Distributive Contribution Method. *J. Chem. Eng. Data* **2012**, *57*, 169−189.

(56) Gao, W.; Robinson, R. L., Jr.; Gasem, K. A. M. Improved correlations for heavy n-paraffin physical properties. *Fluid Phase Equilib.* **2001**, *179*, 207−216.

(57) Lashkarbolooki, M.; Hezave, A. Z.; Bayat, M.; Khademi, M. H.; Vaferi, B. A simple correlation for prediction of thermal conductivity of liquid hydrocarbons and aromatics. *J. Theor. Comput. Chem.* **2016**, *15*, 1650065.

(58) Růžička, V., Jr.; Zábranský, M.; Majer, V. Heat capacities of organic compounds in liquid state II. C1 to C18 n-alkanes. *J. Phys. Chem. Ref. Data* **1991**, *20*, 405−444.

(59) Štejfa, V.; Fulem, M.; Růžička, K. First-principles calculation of ideal-gas thermodynamic properties of long-chain molecules by R1SM approach-Application to n-alkanes. *J. Chem. Phys.* **2019**, *150*, 224101.

(60) Wu, J.; Ning, H.; Xu, X.; Ren, W. Accurate entropy calculation for large flexible hydrocarbons using a multi-structural 2-dimensional torsion method. *Phys. Chem. Chem. Phys.* **2019**, *21*, 10003−10010.

(61) Toscani, S.; Szwarc, H. Two Empirical Equations of State for Liquids To Improve p, V, T Data Representation and Physical Meaning. *J. Chem. Eng. Data* **2004**, *49*, 163−172.

(62) Faden, M.; Höhlein, S.; Wanner, J.; König-Haagen, A.; Brüggemann, D. Review of Thermophysical Property Data of Octadecane for Phase-Change Studies. *Materials* **2019**, *12*, 2974.

(63) Abdulagatov, A. I.; Stepanov, G. V.; Abdulagatov, I. M. Vapor-pressure for the pure fluids from calorimetric measurements near the critical point. *Fluid Phase Equilib.* **2003**, *209*, 55−79.

(64) Yagofarov, M. I.; Sokolov, A. A.; Bolmatenkov, D. N.; Solomonov, B. N. Relationship between the heat capacity change on vaporization of normal and branched alkanes and the vaporization enthalpy and its prediction as a function of temperature. *J. Chem. Thermodyn.* **2021**, *163*, 106586.

(65) Costa, J. C. S.; Mendes, A.; Santos, L. M. N. B. F. Chain Length Dependence of the Thermodynamic Properties of n-Alkanes and their Monosubstituted Derivatives. *J. Chem. Eng. Data* **2018**, *63*, 1−20.

(66) Costa, J. C. S.; Santos, L. M. N. B. F. Chain-Length Dependence of the Thermodynamic Behavior of Homologous α,ω-Disubstituted Alkanes. *J. Chem. Eng. Data* **2019**, *64*, 2229−2246.

(67) Kuznetsov, N.; Frolov, S. Heat Capacities and Enthalpies of Normal Alkanes in an Ideal Gas State. *Energies* **2021**, *14*, 2641.

(68) Guan, C.; Lu, M.; Zeng, W.; Yang, D.; Han, D. Prediction of Standard Enthalpies of Formation Based on Hydrocarbon Molecular Descriptors and Active Subspace Methodology. *Ind. Eng. Chem. Res.* **2020**, *59*, 4785−4791.

(69) Yalamanchi, K. K.; van Oudenhoven, V. C. O.; Tutino, F.; Monge-Palacios, M.; Alshehri, A.; Gao, X.; Sarathy, S. M. Machine Learning To Predict Standard Enthalpy of Formation of Hydrocarbons. *J. Phys. Chem. A* **2019**, *123*, 8305−8313.

(70) Meier, R. J. Group Contribution Revisited: The Enthalpy of Formation of Organic Compounds with "Chemical Accuracy". *ChemEngineering* **2021**, *5*, 24.

(71) Crepnjak, M.; Pleteršek, P. Ž. Correlation between Heat of Formation and Fifth Geometric-Arithmetic Index. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2019**, *27*, 559−565.

(72) Cao, C.-Z.; Liu, J.-L. Correlation between the Ionization Potential and Enthalpy of Formation for Alkanes. *Acta Phys.-Chim. Sin.* **2007**, *23*, 955−958.

(73) Patel, P.; Wilson, A. K. Domain-based local pair natural orbital methods within the correlation consistent composite approach. *J. Comput. Chem.* **2020**, *41*, 800−813.

(74) Wu, Y.; Tang, K. Estimation of the enthalpy of formation for monosubstituted alkanes by ^{13}C NMR chemical shift. *J. Phys. Org. Chem.* **2020**, *33*, No. e4102.

(75) Haseli, Y. Interrelations between standard entropy, formation enthalpy and boiling temperature of hydrocarbons. *Fuel* **2020**, *280*, 118541.

(76) Santos, R. C.; Leal, J. P. A Review on Prediction Methods for Molar Enthalpies of Vaporization of Hydrocarbons: The ELBA Method as the Best Answer. *J. Phys. Chem. Ref. Data* **2012**, *41*, 043101.

(77) Bolmatenkov, D. N.; Yagofarov, M. I.; Notfullin, A. A.; Solomonov, B. N. Calculation of the vaporization enthalpies of alkylaromatic hydrocarbons as a function of temperature from their molecular structure. *Fluid Phase Equilib.* **2022**, *554*, 113303.

(78) Umnahanant, P.; Zafar, A.; Kankala, V.; Chickos, J. Vapor pressure and vaporization enthalpy studies of (+)-longifolene, (−)-isolongifolene and β-myrcene by correlation gas chromatography. *J. Chem. Thermodyn.* **2019**, *131*, 583−591.

(79) Alam, M. S.; Nikolova, I.; Singh, A.; MacKenzie, A. R.; Harrison, R. M. Experimental vapour pressures of eight n-alkanes (C17, C18, C20, C22, C24, C26, C28 and C31) measured at ambient temperatures. *Atmos. Environ.* **2019**, *213*, 739−745.

(80) Audran, G.; Marque, S. R. A.; Siri, D.; Santelli, M. Enthalpy of Combustion on n-Alkanes. Quantum Chemical Calculations up to n-$C_{60}H_{122}$ and Power Law Distributions. *ChemistrySelect* **2018**, *3*, 9113−9120.

(81) Manion, J. A. Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons. *J. Phys. Chem. Ref. Data* **2002**, *31*, 123−172.

(82) Haarmann, N.; Siewert, R.; Samarov, A. A.; Verevkin, S. P.; Held, C.; Sadowski, G. Thermodynamic Properties of Systems Comprising Esters: Experimental Data and Modeling with PC-SAFT and SAFT-γ Mie. *Ind. Eng. Chem. Res.* **2019**, *58*, 6841−6849.

(83) Cao, C.-T.; Yuan, H.; Cao, C. New concept of organic homorank compounds and its application in estimating enthalpy of formation of mono-substituted alkanes. *J. Phys. Org. Chem.* **2015**, *28*, 266−280.

(84) van Speybroeck, V.; Gani, R.; Meier, R. J. The calculation of thermodynamic properties of molecules. *Chem. Soc. Rev.* **2010**, *39*, 1764−1779.

(85) Zafar, A.; Chickos, J. The vapor pressure and vaporization enthalpy of squalene and squalane by correlation gas chromatography. *J. Chem. Thermodyn.* **2019**, *135*, 192−197.

(86) Hofman, T. Prediction of Thermodynamic Properties of the Systems Formed by n-Alkanes, Aliphatic Monoethers, and 1-Chloroalkanes, Using a Cell−Hole Group Contribution Model. *J. Phys. Chem. B* **2004**, *108*, 2383−2397.

(87) Santak, P.; Conduit, G. Predicting physical properties of alkanes with neural networks. *Fluid Phase Equilib.* **2019**, *501*, 112259.

(88) Hoffmann, D.; Castier, M.; Paredes, M. L. L.; Mattedi, S. Liquid Phase Density, Sound Speed, and Vapor Pressure of Linear Alkanes Using the Mattedi-Tavares-Castier Equation of State. *Ind. Eng. Chem. Res.* **2019**, *58*, 6767−6777.

(89) Koutek, B.; Fulem, M.; Mahnel, T.; Šimáček, P.; Růžička, K. Extracting Vapor Pressure Data from Gas-Liquid Chromatography

(90) Aparicio-Martínez, S.; Hall, K. R. Use of PC-SAFT for Global Phase Diagrams in Binary Mixtures Relevant to Natural Gases. 1. n-Alkane + n-Alkane. *Ind. Eng. Chem. Res.* **2007**, *46*, 273−284.

(91) Chen, Z.; Yao, Z.; Li, Y.; Cao, K.; Huang, Z. Prediction of Vapor−Liquid Equilibrium at High Pressure Using a New Excess Free Energy Mixing Rule Coupled with the Original UNIFAC Method and the SRK Equation of State. *Ind. Eng. Chem. Res.* **2009**, *48*, 6836−6845.

(92) dos Ramos, M. C.; Blas, F. J. Examination of the Excess Thermodynamic Properties of n-Alkane Binary Mixtures: A Molecular Approach. *J. Phys. Chem. B* **2005**, *109*, 12145−12153.

(93) Atabati, M.; Emamalizadeh, R. A Quantitative Structure Property Relationship for Prediction of Flash Point of Alkanes Using Molecular Connectivity Indices. *Chin. J. Chem. Eng.* **2013**, *21*, 420−426.

(94) Mathieu, D. Inductive modeling of physico-chemical properties: Flash point of alkanes. *J. Hazard. Mater.* **2010**, *179*, 1161−1164.

(95) Nieto-Draghi, C.; Fayet, G.; Creton, B.; Rozanska, X.; Rotureau, P.; de Hemptinne, J.-C.; Ungerer, P.; Rousseau, B.; Adamo, C. A General Guidebook for the Theoretical Prediction of Physicochemical Properties of Chemicals for Regulatory Purposes. *Chem. Rev.* **2015**, *115*, 13093−13164.

(96) Wilhelmsen, Ø.; Aasen, A.; Skaugen, G.; Aursand, P.; Austegard, A.; Aursand, E.; Gjennestad, M. A.; Lund, H.; Linga, G.; Hammer, M. Thermodynamic Modeling with Equations of State: Present Challenges with Established Methods. *Ind. Eng. Chem. Res.* **2017**, *56*, 3503−3515.

(97) Palatinus, J. A.; Sams, C. M.; Beeston, C. M.; Carroll, F. A.; Argenton, A. B.; Quina, F. H. Kinney Revisited: An Improved Group Contribution Method for the Prediction of Boiling Points of Acyclic Alkanes. *Ind. Eng. Chem. Res.* **2006**, *45*, 6860−6863.

(98) Mukwembi, S.; Nyabadza, F. A New Model for Predicting Boiling Points of Alkanes. *Sci. Rep.* **2021**, *11*, 24261.

(99) Yuan, H.; Cao, C. Topological Indices Based on Vertex, Edge, Ring, and Distance: Application to Various Physicochemical Properties of Diverse Hydrocarbons. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 501−512.

(100) Kontogeorgis, G. M.; Dohrn, R.; Economou, I. G.; de Hemptinne, J.-C.; ten Kate, A.; Kuitunen, S.; Mooijer, M.; Žilnik, L. F.; Vesovic, V. Industrial Requirements for Thermodynamic and Transport Properties: 2020. *Ind. Eng. Chem. Res.* **2021**, *60*, 4987−5013.

(101) Cao, C.-T.; Cao, C. General Equation to Express Changes in the Physicochemical Properties of Organic Homologues. *ACS Omega* **2022**, *7*, 26670−26679.

(102) Yuan, H.; Cao, C. Topological Indices Based on Vertex, Edge, Ring, and Distance: Application to Various Physicochemical Properties of Diverse Hydrocarbons. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 501−512.

(103) Cao, C.; Liu, S.; Li, Z. On Molecular Polarizability: 2. Relationship to the Boiling Point of Alkanes and Alcohols. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 1105−1111.

(104) *CRC Handbook of Chemistry and Physics*, 91st ed.; Haynes, W. M., Ed.; CRC Press, 2011; pp 6−58, 6−73, 10−199, 10−216, 5−68.

(105) Chenzhong, C.; Zhiliang, L. Molecular Polarizability. 1. Relationship to Water Solubility of Alkanes and Alcohols. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 1−7.

(106) Cai, G.; Liu, Z.; Zhang, L.; Zhao, S.; Xu, C. Quantitative Structure-Property Relationship Model for Hydrocarbon Liquid Viscosity Prediction. *Energy Fuels* **2018**, *32*, 3290−3298.

(107) Wu, Y.; Cao, C.; Yuan, H. Enthalpies Estimation of Formation of Monosubstituted Alkanes by Interaction Potential Index. *Chin. J. Chem. Phys.* **2012**, *25*, 153−160.

(108) Qu, C.; Kearsley, A. J.; Schneider, B. I.; Keyrouz, W.; Allison, T. C. Graph Convolutional Neural Network Applied to the Prediction of Normal Boiling Point. *J. Mol. Graph. Model.* **2022**, *112*, 108149.