Generalized Vapor Pressure Nomogram for Organic Liquids

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A new comparative method for correlating the vapor pressure of organic liquids, in which the vapor pressure curves of normal paraffin homolog are taken as reference, is proposed. Introduction of two parameters, the "effective carbon number," n_o^* and the "polar number," s, makes it possible to specify the vapor pressure curve of any organic liquid. Vapor pressure nomograms containing $n_o^* - s$ network are constructed. A simple empirical method for evaluating n_o^* of mono-substituted alkane homologs from their molecular structure is also proposed.

RAPID AND ACCURATE estimation of the boiling point or vapor pressure of organic liquids is essential in various kinds of chemical engineering processes such as distillation. If abundant boiling point data are available for wide ranges of external pressure, one can determine the probable value of three constants of the Antoine equation, construct the Cox chart (*2*), or make some other graphical representations (*4, 10*). Then the boiling point at any external pressure or, inversely, the vapor pressure at any temperature can be calculated or read with sufficient accuracy.

However, when the available experimental data are limited or unknown, these methods are of no use or, at least, accurate estimation becomes difficult. It is thus desirable to establish a general method for estimating a vapor pressure curve using only a few data. Vapor pressure nomograms proposed by Lippincott and Lyman (*5*) or Reckhard (*11*) may be used for this purpose. In the former nomogram, all organic compounds are classified into several groups for which specific scales are given on the chart. No general guidance is given for this classification. On the other hand, constant b in the latter is introduced on the assumption that the heat of vaporization is independent of the temperature. This assumption is inadequate for estimation in a wide range of external pressures.

This article presents a general method for arranging the vapor pressure data of organic liquids. If the vapor pressure data of normal paraffin homologs are taken as reference, that of other organic compounds can be sepecified by two parameters,—the "effective carbon number," n_o^*, and the "polar number," s. By combining these parameters with the equations and nomograms proposed in a previous study (*9*), new generalized nomograms are constructed which make it possible to estimate the boiling point, vapor pressure, and the heat and entropy of vaporization at normal boiling point. In addition, the structural variations in n_o^* and s of mono-substituted alkanes are throughly studied, and an empirical method for estimating n_o^* of these compounds only from the knowledge of structural formula is presented.

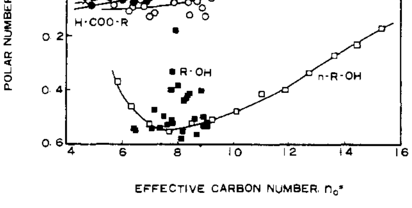

Figure 1. Determination of effective carbon number n^*

EFFECTIVE CARBON NUMBER AND POLAR NUMBER

To express the vapor pressure curve of various kinds of organic liquids by taking those of the normal paraffin homolog as reference, the following method is adopted. The boiling points of normal paraffins, T_b, are plotted against the number of carbon atoms, n, and a family of curves for different external pressures is obtained. For this purpose one can utilize reliable boiling point data given by API Research Project 44 (*1*) for the normal paraffins of carbon number 1 to 20. By reading the boiling point of a given compound on these curves as illustrated in Figure 1, one can obtain a set of values for "effective carbon number" at varying pressure. As already shown (*7, 9, 14*), this effective carbon number is almost independent of external pressure for isoparaffins, olefins, or acetylenic hydrocarbons. For other organic compounds, this number changes with pressure and cannot be regarded as a constant characteristic to the compound under consideration. However, if n^* is plotted against log P, a straight line is obtained in most cases as shown in Figure 2. One can thus write

$$n^* = n_o^* + s \log P \tag{1}$$

where n_o^* is the effective carbon number at normal boiling point, s is a constant called the "polar number," and P is the external pressure in atmosphere.

This suggests that the vapor pressure curve of any organic liquid can be specified by two parameters, n_o^* and s, related to the curves for normal paraffins. By combining this set of parameters and the $T_b - n$ plot, the vapor pressure curve of organic liquids can be constructed. To predict the boiling point at any pressure, it is convenient to formulate this relationship in an empirical equation or

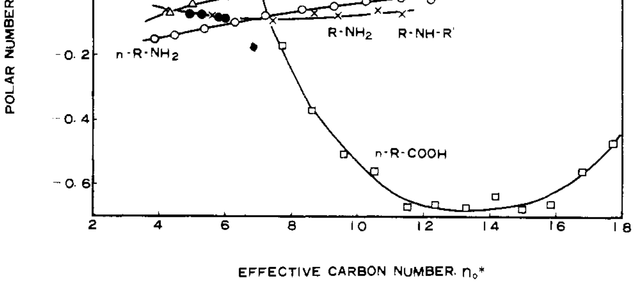

Figure 2. Pressure dependence of n^*

to construct it as a nomograph. It has been shown (*9*) that the vapor pressure curve of aliphatic hydrocarbons is reproduced by the following equation:

$$\frac{1}{T_b} = \frac{0.007824 - 0.00213 \log P + 0.000051 (\log P)^2}{(n^*)^{2/3}} + (0.0005543 - 0.000023 \log P) \quad (2)$$

The values of coefficients of Equation 2 and following equations are slightly different from those in the previous paper (*9*) (see Appendix).

Combining Equation 2 with Equation 1, a new vapor pressure equation for organic liquids is obtained:

$$\frac{1}{T_b} = \frac{0.007824 - 0.00213 \log P + 0.000051 (\log P)^2}{(n_o^* + s \log P)^{2/3}} + (0.0005543 - 0.000023 \log P) \quad (3)$$

The equation for the heat of vaporization, Λ, is then derived by substituting the vapor pressure equation into the Clapeyron equation:

$$\Lambda = RT^2 (d \ln P/dT) \quad (4)$$

After a simple calculation, the following equation is derived:

$$\Lambda = \frac{2.303\, R\, (n_o^* + s \log P)^{2/3}}{B' + 2C' \log P + \frac{2}{3} s\{[A' - B' \log P - C' (\log P)^2]/(n_o^* + s \log P)\} + E' (n_o^* + s \log P)^{2/3}} \quad (5)$$

where

$$\left.\begin{array}{lll} A' = 0.007824, & C' = 0.000051, & E' = 0.000023, \\ B' = 0.00213, & D' = 0.0005543, & \end{array}\right\} \quad (6)$$

Putting log $P = 0$, i.e., $P = 1$, (atm.), the equation for the heat of vaporization at normal boiling point, $\Lambda°$, is obtained.

$$\Lambda° = 2.303 \frac{R}{B'} \frac{(n_o^*)^{2/3}}{1 + E'/B' \cdot (n_o^*)^{2/3} + \frac{2}{3} \cdot A'/B' \cdot (s/n_o^*)} \quad (7)$$

$$= \frac{2.149\, (n_o^*)^{2/3}}{1 + 0.0110\, (n_o^*)^{2/3} + 2.450\, (s/n_o^*)} \text{ [kcal./mole]} \quad (8)$$

Furthermore, Equation 3 reduces to:

$$T_b° = \frac{127.82\, (n_o^*)^{2/3}}{1 + 0.07085\, (n_o^*)^{2/3}} \text{ [° K.]} \quad (9)$$

when $P = 1$. This equation gives the normal boiling point, $T_b°$. Combining this equation with Equation 8, the entropy of vaporization at normal boiling point, $\Delta S°$, the so-called Trouton ratio, is obtained:

$$\Delta S° = \frac{\Lambda°}{T_b°} = 16.82 \frac{1 + 0.07085\, (n_o^*)^{2/3}}{1 + 0.0110\, (n_o^*)^{2/3} + 2.450\, (s/n_o^*)} \text{ [cal./° C. mole]} \quad (10)$$

If sufficient vapor pressure data are available, the most probable values of n_o^* and s for any organic compound can be evaluated. Table I presents the estimated value of n_o^* and s for 38 typical compounds, among which are some simple inorganic compounds such as HCl and NH_3. These compounds were selected from examples in the literature (*12*). As explained below, two boiling point values are sufficient to determine the approximate values of n_o^* and s.

NOMOGRAMS

For the purpose of rapid estimation, the new equation presented above is arranged in nomographic form. Here three nomograms are constructed.

Vapor Pressure Nomogram. The basic equation for the vapor pressure nomogram is Equation 3. Although this equation contains four variables, T, P, n_o^* and s, it reduces to Equation 2 for paraffin hydrocarbons in the special case that s is equal to zero. A previous nomogram (*9*), in which three scales, T-axis, P-axis, and n^*-axis were incorporated, was based on Equation 2. The new nomogram based on Equation 3 has the same form, the only difference being that the n^*-axis is replaced by an n_o^*- s network. This network contains the original n^*-axis as the s = line.

From the definition of two parameters, n_o^* and s, construction of the n_o^*- s network is straightforward. As is seen in Equation 9, n_o^* has one-to-one correspondence to the normal boiling point. Thus, the iso-n_o^* lines are given by a group of straight lines drawn radially from the point of $P = 1$ (atm.) on the P-axis. The iso-s lines are not given by straight lines except for the $s = 0$ line, but the construction of the iso-s lines are easily performed as follows. First, two groups of straight lines are drawn radially from $P = 1$ (atm.) and from $P = 0.1$ (atm.) to pass through each point on the n^*-axis.—*i.e.*, $s = 0$ line. Then, on each of these straight lines from $P = 1$, s-scales are determined

Table I. Effective Carbon Number n_o^* and Polar Number s of Typical Organic and Inorganic Compounds

Compound	n_o^*	s	Data Source
Cyclopentane	5.39	+0.01	(*13*)
Cyclohexane	6.40	+0.04	(*13*)
Methylcyclopentane	6.10	+0.02	(*13*)
Benzene	6.36	−0.02	(*13*)
Ethylbenzene	8.40	+0.04	(*13*)
o-Xylene	8.74	+0.06	(*13*)
m-Xylene	8.53	+0.05	(*13*)
Naphthalene	12.09	+0.25	(*13*)
Fluorobenzene	6.54	−0.001	(*13*)
Bromobenzene	9.24	+0.10	(*13*)
Chlorobenzene	8.26	+0.06	(*13*)
Iodobenzene	10.67	+0.17	(*13*)
Phenol	10.36	−0.32	(*13*)
p-Cresol	11.28	−0.30	(*13*)
Methanol	5.87	−0.34	(*1*)
n-Propyl alcohol	6.96	−0.50	(*1*)
Isopropyl alcohol	6.44	−0.51	(*1*)
Dimethyl ether	3.43	−0.03	(*13*)
Acetone	5.60	−0.07	(*1*)
Acetic acid	7.71	−0.11	(*13*)
Isobutyric acid	9.16	−0.28	(*13*)
Methyl formate	4.88	−0.10	(*13*)
Ethyl acetate	6.27	−0.12	(*13*)
Ethylamine	4.47	−0.14	(*6*)
Diethylamine	5.59	−0.08	(*6*)
Aniline	10.45	−0.08	(*13*)
Acetonitrile	6.43	−0.05	(*6*)
Chloroform	5.77	−0.03	(*13*)
Carbon tetrachloride	6.28	+0.02	(*13*)
Ethyl bromide	5.07	−0.02	(*6*)
Ethyl mercaptan	4.97	−0.04	(*1*)
Diethyl sulfide	6.78	−0.01	(*1*)
Phosgene	4.23	−0.04	(*13*)
Ammonia	3.20	−0.15	(*13*)
Carbon disulfide	5.30	+0.05	(*13*)
Chlorine	3.19	−0.02	(*13*)
Water	7.06	−0.33	(*13*)
Hydrogen chloride	2.08	−0.06	(*13*)

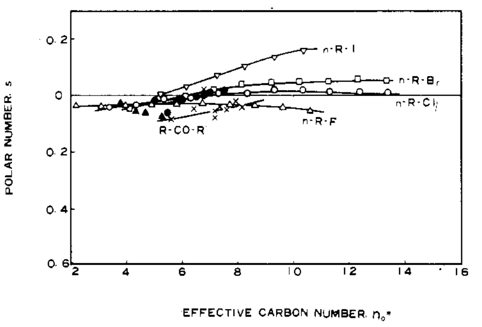

Figure 3. Construction of $n_o^* - s$ network

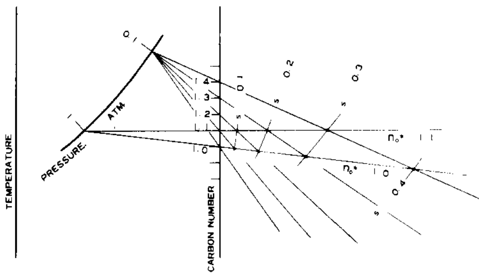

Figure 4. Generalized vapor pressure nomogram I (nomogram 1)

successively as each of intersecting points to the straight lines from $P = 0.1$. Finally, the iso-s line is obtained by connecting these intersecting points. Figure 3 illustrates the procedure.

Two nomograms thus constructed are presented as Figures 4 and 5. Corresponding to their parent nomograms (*9*), nomogram 1 (Figure 4) covers the temperature range from −175° to +150° C., while nomogram 2 (Figure 5) covers 0° to 550° C. In the n_o^*- s network of the two nomograms, the scale of n_o^* extends from 1.8 to 15 and s from +0.2 to −1.0. Almost all important organic liquids will come within either of the two networks. As for other compounds whose position on the nomogram is off the network scales, a conventional method (described below) for determining their position on nomogram can be used.

Using these two nomograms, one can read the normal and other boiling points or the vapor pressure at every temperature. The critical point and the melting point on the nomograms can be used only for the aliphatic hydrocarbons (*9*).

Heat of Vaporization at Normal Boiling Point Nomogram. The basic equation for this nomogram is Equation 8, which may be rewritten as:

$$f(\Lambda^\circ) + g(s) \times h(n_o^*) = \phi(n_o^*) \qquad (11)$$

with

$$f(\Lambda^\circ) = \frac{1}{\Lambda^\circ}, \qquad g(s) = -s,$$

$$h(n_o^*) = \frac{1.142}{(n_o^*)^{5/3}} \qquad \phi(n_o^*) = \frac{1 + 0.00512\,(n_o^*)^{2/3}}{2.128\,(n_o^*)^{2/3}} \qquad (12)$$

This three-variable equation can be readily represented as a nomogram of the same type as the vapor pressure nomogram. The Λ° nomogram (nomogram 3) based on Equation 11 is shown in Figure 6.

In the nomogram, some empirical scale corrections have been made because the values of Λ° calculated by Equation 8 are almost always lower than those observed. This deviation is eliminated by ajusting s to a slightly larger value if it is negative and to a smaller value if positive. This point is discussed later. In addition, the n_o^* scale is corrected to reproduce precisely the literature values (*1*) of Λ° for normal paraffins.

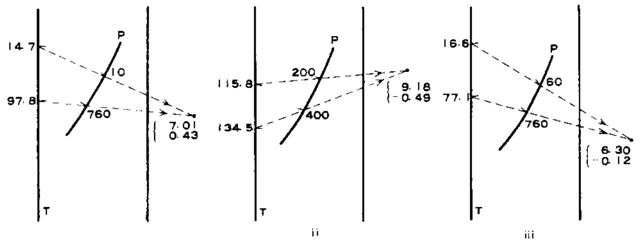

Figure 5. Generalized vapor pressure nomogram II (nomogram 2)

Entropy of Vaporization at Normal Boiling Point Nomogram. The entropy of vaporization at normal boiling point, ΔS°, the so-called Trouton ratio, is given by Equation 10, which may be rewritten as:

$$f(\Delta S^\circ) + g(s) \times h(n_o^*) = \phi(n_o^*) \qquad (13)$$

with

$$f(\Delta S^\circ) = (1/\Delta S^\circ), \qquad g(s) = -s,$$

$$h(n_o^*) = \frac{0.1457}{[1 + 0.07033\,(n_o^*)^{2/3}]\,n_o^*},$$

$$\phi(n_o^*) = 0.05995\frac{1 + 0.00512\,(n_o^*)^{2/3}}{1 + 0.07033\,(n_o^*)^{2/3}} \qquad (14)$$

Based on Equation 13, the ΔS° nomogram (nomogram 4) which is of the same type as the Λ° nomogram, is prepared as in Figure 7. Empirical corrections in s- and n_o^*-scales, as explained above, have also been made.

COMPARISON WITH EXPERIMENTAL DATA

To test the utility of the nomograms presented above, comparison is made between observed and estimated values. Since the accuracy of estimation depends on the extent of available boiling point data, two limiting cases are considered.

Let us first investigate the estimation of general boiling points, Λ° and ΔS° when wide ranges of boiling point data are available. In this case, the most probable values of n_o^* and s are already known, and the estimations are readily performed. As an example, the estimated values of the boiling points below 1 atm., Λ° and ΔS° for all compounds cited in Table I are compared with the observed values (*1, 6, 13*). The results are summarized in Table II. For

Table II. Summary of Experimental Test of Present Nomograms

Property	No. of Points Tested	Av. Dev.	Data Source
T_b^a	234	±0.81° C.	(*1, 6, 13*)
Λ°	38	±0.17 Kcal./mole ±2.44%	(*12*)
ΔS°	38	±0.46 Cal./° C. mole ±2.22%	(*12*)

[a] Below 1 atm.

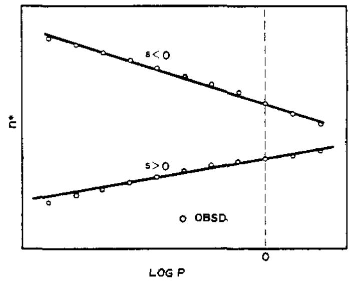

Figure 6. Heat of vaporization at normal boiling point nomogram (nomogram 3)

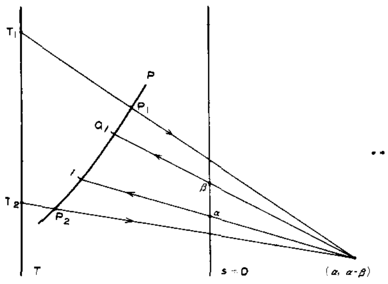

Figure 7. Entropy of vaporization at normal boiling point nomogram (nomogram 4)

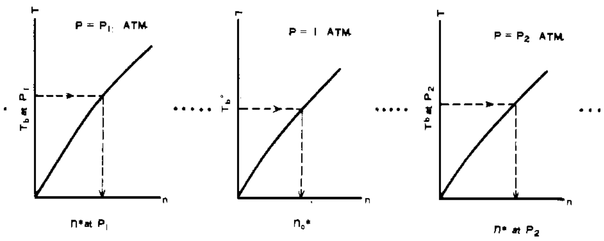

Figure 8. Determination of n_0 and s on nomogram

pressures ranging higher than 1 atm., the average deviation of estimated from observed T_b value becomes somewhat large. However, deviation hardly exceeds ±5° C. except for highly polar or associated liquids such as aliphatic acids or alcohols.

Second, it is often necessary in practice to estimate vapor pressure or boiling point when only a few boiling point data are available. Only two boiling points are sufficient to evaluate n_o^* and s of these compounds and thus make it possible to read the whole vapor pressure curve on nomograms 1 and 2. As an illustration, let us estimate the boiling points of *n*-propyl alcohol, isobutyric acid, and ethyl acetate when two of the boiling points shown in Figure 8 are known. First, n_o^* and s of these compounds must be determined. This is done easily on nomogram 2 by the procedure shown schematically in Figure 8. Using these n_o^* and s values, the boiling points at any external pressure are read on nomograms 1 and 2, and the results are compared with the observed values in Table III. The table shows that the agreement between observed and estimated values is satisfactory, but the deviation increases in the case when the range of estimation for the associated liquids is extrapolated beyond the pressure range between two known boiling points (as for isobutyric acid).

If one boiling point is given or the boiling point data are unknown, n_o^* and/or s must be evaluated. As shown below, evaluation of n_o^* only from the knowledge of structural formula is possible for some kinds of organic compounds such as mono-substituted alkanes.

For the high boiling point liquids whose n_o^* is larger than 15, their position on nomogram is off the network scales. But the position and the values of n_o^* and s can be determined from two known boiling point data, (P_1, T_1) and (P_2, T_2). Figure 9 shows this procedure, by which n_o^* is given by α and s by $\alpha - \beta$.

THE NATURE OF POLAR NUMBER *s*

As indicated, the accuracy of estimation by the present nomograms is, as a whole, highly satisfactory. The results for the boiling points at reduced pressures are accurate so long as the pressure dependence of n^* can be expressed by Equation 1. However, the deviation of estimated from experimental values in the high pressure region suggests the inapplicability of Equation 1 for a wide range of external pressure. To express the pressure dependence of n^* more precisely, Equation 1 should be replaced by the following general equation:

$$n^* = n_o^* + s \log P + t (\log P)^2 + \cdots \qquad (15)$$

where t is a constant characteristic to the compound under

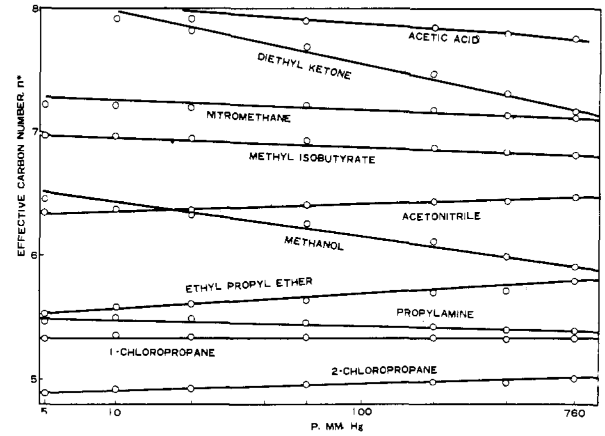

Figure 9. Determination of position representing a compound on nomogram

Table III. Results of Estimation when Two Boiling Points are Available

Compound	760	400	100	60	10	5	1
	T_b, ° C., at 1 to 760 Mm. of Hg						
n-Propyl alcohol							
Obsd.	97.8[a]	82.0	52.8	43.5	14.7[a]	+5.0	−15.0
Calcd.	97.8[a]	81.0	51.5	42.0	14.7[a]	+5.8	—
Isobutyric acid							
Obsd.	145.5	134.5[a]	98.0	86.3	51.2	39.3	14.7
Calcd.	155	134.5[a]	101	89.5	58.0	47.0	26.5
Ethyl acetate							
Obsd.	77.1[a]	59.3	27.0	+16.6[a]	−13.5	−23.5	−43.3
Calcd.	77.1[a]	58.0	26.5	+16.6[a]	−15	−25	−44

[a] Boiling points for which data are available.

consideration. In the estimation of boiling points, t may be neglected. But this approximation fails in the Λ° estimation. As already noted, the calculated value of Λ° by Equation 8 is always lower than the observed value. This is because s is overestimated when it is positive and underestimated when negative. Figure 10 explains this situation schematically. If the third parameter t is adopted in addition to n_o^* and s, more accurate reproduction of the vapor pressure curve may be possible, though expression by nomogram becomes difficult. Accordingly, in the present method, t is regarded as zero, and instead an empirical correction is made on the s-scale of nomograms 3 and 4.

Inspection of s value in Table I leads to the following observation.

1. For highly polar or associated liquids, such as aliphatic acids, alcohols, or phenols s has a large negative value.
2. For nonpolar liquids, such as benzene or carbon tetrachloride, s is nearly equal to zero.
3. Generally speaking, aromatic compounds have a positive s value.

In this connection, let us investigate the thermodynamic character of s. As is evident from Equation 1, s is defined by

$$s = (\partial n^*/\partial \log P)_{P=1} \qquad (16)$$

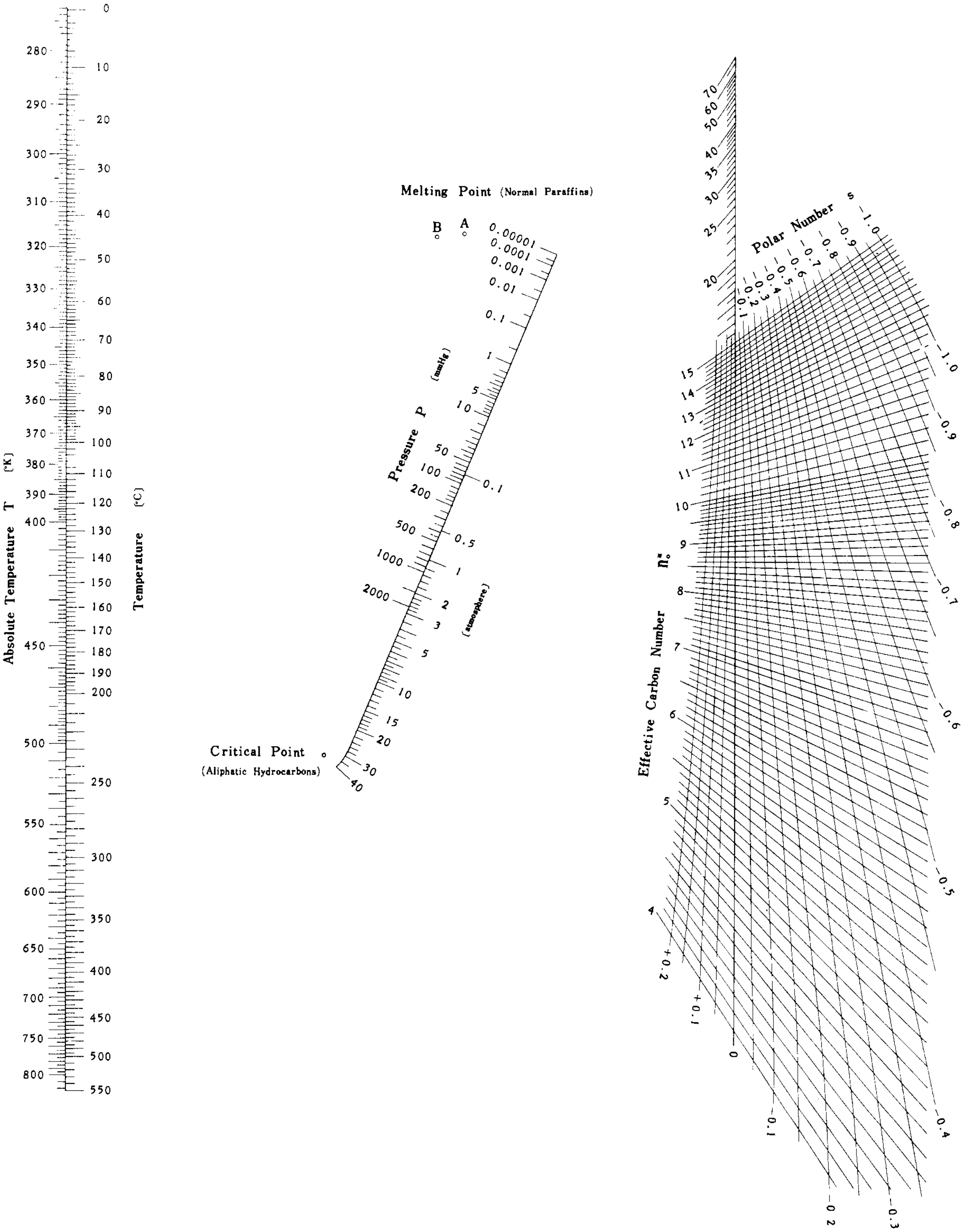

Figure 10. Detailed analysis of n^* vs. log P data

If the right-hand side of Equation 3 is written as $A(\log P)$, n^* is expressed as:

$$n^* = [TA(\log P)]^{3/2} = [T(\log P)A(\log P)]^{3/2} \qquad (17)$$

Then, Equation 16 should be rewritten as:

$$s = \left[\frac{\partial n^*}{\partial T}\ \frac{\partial T}{\partial \log P} + \frac{\partial n^*}{\partial A(\log P)}\ \frac{\partial A(\log P)}{\partial \log P}\right]_{p=1} \qquad (18)$$

Substituting Equation 17 into Equation 18, the following relationship can be derived after some simple calculations:

$$s = 2.303 \times 3/2 \times R \times n_o^* (1/\Delta S^\circ - 1/\Delta S_p^\circ) \qquad (19)$$

where ΔS_p° is the entropy of vaporization at normal boiling point of the corresponding normal paraffin whose carbon number is equal to n_o^* of the compound under consideration.

Thus the physical meaning of the polar number s becomes clear, and the above observations on the values of s can be explained reasonably: s has a large negative value for the liquids having large Trouton ratio. To ascertain the validity of the above derivation, the value of s calculated by Equation 19 is compared to those from the vapor pressure data. The results are summarized in Table IV, from which a close agreement is obtained between two evaluated s values. A significant discrepancy appeared in the case of methanol owing to the fact that the pressure dependence of n^* for methanol is reproduced by Equation 15. In fact, s and t are estimated to be -0.417 and -0.077 by the method of least squares, showing good agreement with the above value from Equation 19. Such discrepancy is negligible except for the lower members of alcohols or some other associated liquids.

n_o^* AND s FOR MONO-SUBSTITUTED ALKANES

The utility of the nomograms presented above will be remarkably increased, if a general method for evaluating n_o^* and s uses only the structural formula or other known properties inherent to the compound. This is a tremendously difficult problem. In fact, only poor results have been obtained by the existing general methods for the estimation of normal boiling point (*12*). So, it is necessary to establish empirical equations which apply only to a limited number of homologous compounds. In this section, the structural variation in the values of n_o^* and s of the homologous series of mono-substituted alkanes is throughly examined, and empirical equations for estimating n_o^* are proposed.

Empirical Equations for Calculating n_o^*. For the following 14 homologous series of mono-substituted alkanes, n_o^* can be calculated by the equations presented below.

ALKYL HALIDE *RX*

Primary
F $n_o^* = n_p + (1.08 - 0.052\, n_p)$ (20a)
Cl $n_o^* = n_p + 2.35$ (20b)
Br $n_o^* = n_p + (3.02 + 0.026 n_p)$ (20c)
I $n_o^* = n_p + (3.89 + 0.071 n_p)$ (20d)

Secondary
F $n_o^* = 0.898\, n_p + 1.08$ (21a)
Cl $n_o^* = n_p + 2.00$ (21b)
Br $n_o^* = 1.030\, n_p + 2.65$ (21c)
I $n_o^* = 1.10\, n_p + 3.39$ (21d)

Tertiary
F $n_o^* = 0.876\, n_p + 1.08$ (22a)
Cl $n_o^* = n_p + 1.79$ (22b)
Br $n_o^* = 1.020\, n_p + 2.37$ (22c)
I $n_o^* = 1.14\, n_p + 2.82$ (22d)

ALKANOLS ROH

Primary
Secondary $n_o^* = n_p + [1/(0.0178\, n_p + 0.194)]$ (23a)
Tertiary $n_o^* = n_p + [1/(0.0336\, n_p + 0.191)]$ (23b)
$n_o^* = n_p + [1/(0.0586\, n_p + 0.141)]$ (23c)

ALKYLTHIOLS RSH

Primary $n_o^* = 1.032\, n_p + 2.88$ (24a)
Secondary $n_o^* = 1.024\, n_p + 2.43$ (24b)
Tertiary $n_o^* = 1.066\, n_p + 1.92$ (24c)

ALKANALS RCHO

Primary $n_o^* = 1.072\, n_p + 3.47$ (25a)
Secondary $n_o^* = 1.092\, n_p + 3.15$ (25b)
Tertiary $n_o^* = 1.066\, n_p + 2.74$ (25c)

NITROALKANES RNO_2

Primary $n_o^* = 0.812\, n_p + 5.92$ (26a)
Secondary $n_o^* = 0.672\, n_p + 5.83$ (26b)
Tertiary $n_o^* = 0.850\, n_p + 4.89$ (26c)

ALKYL CYANIDES RCN

Primary $n_o^* = n_p + [1/(0.0017 n_p + 0.212)]$ (27)

ALKANOIC ACIDS RCOOH

Primary $n_o^* = 0.903\, n_p + 6.87$ (28a)
Secondary $n_o^* = 0.890\, n_p + 6.53$ (28b)
Tertiary $n_o^* = 0.966\, n_p + 6.01$ (28c)

In Equations 20a to 28c, n_p is the carbon number or the effective carbon number of the corresponding parent paraffin, RH. For the branched alkanes, n_p can be calculated by the following equation (*7, 14*):

$$n_p = n - \sum \overset{|}{-\mathrm{C}-}(0.28 - 0.06\, c_2 + 0.06\, c_3)$$
$$- \sum \underset{|}{\overset{|}{-\mathrm{C}-}}(0.73 - 0.14\, c_2 + 0.05\, c_3) \qquad (29)$$

where n is the number of the carbon atoms in the molecule and the two summations extend over all the structural units containing tertiary or quaternary carbon atoms, respectively. c_2 and c_3 are defined below.

ALKYL ETHERS ROR′

$$n_o^* = (n_p + 1) + 0.40 - 0.20\, c_2 - 0.16\, c_3 \qquad (30)$$

Table IV. Evaluation of s

Compound	n_o^*	ΔS° Cal./° C. Mole	ΔS°_p[a] Cal./° C. Mole	s Calcd.[b]	s Obsd.[c]
Methylcyclopentane	6.10	20.05	20.20	+0.015	+0.02
Benzene	6.36	20.82	20.25	−0.059	−0.02
Methanol	5.87	25.14	20.14	−0.398	−0.34
Acetone	5.60	20.97	20.07	−0.082	−0.07
Ethyl mercaptan	4.97	20.77	19.91	−0.071	−0.04
Diethyl sulfide	6.78	20.78	20.34	−0.048	−0.01

[a] Values read on ΔS° *vs.* n plot for normal paraffins. [b] Values calculated by Equation 19. [c] Values estimated from vapor pressure data.

ALKANESULFIDES RSR′

$$n_o^* = (n_p + 1) + 2.04 - 0.14\,c_2 - 0.05\,c_3 \qquad (31)$$

ALKANEDISULFIDES RSSR′

$$n_o^* = (n_p + 1) + 4.41 - 0.16\,c_2 - 0.19\,c_3 \qquad (32)$$

ALKANONES RCOR′

$$n_o^* = (n_p + 1) + 2.60 - 0.24\,c_2 - 0.21\,c_3 - 0.09\,c_4 \qquad (33)$$

PRIMARY AMINES RNH_2

$$n_o^* = (n_p + 1) + 2.85 - 0.44\,c_2 - 0.10\,c_3 - 0.03\,c_4 \qquad (34)$$

SECONDARY AMINES RNHR′

$$n_o^* = (n_p + 1) + 1.19 - 0.28\,c_2 - 0.14\,c_3 - 0.05\,c_4 \qquad (35)$$

ESTERS RCOOR′

$$n_o^* = (n_p + 1) + 3.14 - 0.24\,c_1 - 0.33\,c_2 - 0.16\,c_3 - 0.08\,c_4 \qquad (36)$$

In Equations 30 to 36, n_p is the sum of the number of carbon atoms in both sides of the given substituent, if R- and R′- are the normal alkyl group. But, if any one of the two alkyl groups is branched, $(n_p + 1)$ is given by the effective carbon number of an isoparaffin obtained when the substituent is replaced by a methylene group, $—CH_2—$. The parameters, c's are defined as below.

c_1 = number of the α-carbon atoms to the substituent.
c_2 = number of the second neighbor carbon atoms to the substituent.
c_3 = number of the third neighbor carbon atoms to the substituent.
c_4 = number of the fourth neighbor carbon atoms to the substituent.

The coefficients of the above equations are determined from the available normal boiling point data (*1, 3, 6, 13, 15*). Some of them, for example, those for secondary and tertiary halogens, are quite arbitrary and may require revisions after further compilations of experimental data, since the literature values being referred to are still limited in number.

Sample Calculations. To illustrate the method for calculating n_o^*, it is convenient to present some examples.

n-PROPYL CHLORIDE. Since this contains the primary chloro-group, n_o^* can be calculated by Equation 20b.

$$n_o^* = n_p + 2.35 = 3 + 2.35 = 5.35$$

ISOBUTYL CHLORIDE. The parent paraffin of the alkyl group of this compound is isobutane whose effective carbon number is 3.72, and n_o^* can be calculated also by Equation 20b.

$$n_o^* = n_p + 2.35 = 3.72 + 2.35 = 6.07$$

ETHANOL. n_o^* is calculated by the substitution of $n_p = 2$ into Equation 23a.

$$n_o^* = n_p + [1/(0.0178\,n_p + 0.194)] = 6.36$$

ETHYL PROPYL ETHER, $C^1C_2OC^3C^4C^5$. n_o^* can be calculated by Equation 30. Since both the alkyl groups are normal, n_p is equal to 5 and the second neighbor to —O— is C^1 and C^4, and the third neighbor, C^5. Thus, $c_2 = 2$ and $c_3 = 1$. Then,

$$n_o^* = (n_p + 1) + 0.40 - 0.20\,c_2 - 0.16\,c_3$$

$$n_o^* = 5 + 1 + 0.40 - (0.20 \times 2) - 0.16 = 5.84$$

METHYL ISOBUTYRATE. This compound, $C^1C^2(C^3)COOC^4$, has a branched alkyl group and the corresponding isoparaffin is 2-methylbutane, $C^1C^2(C^3)CC^4$, whose effective carbon number is 4.78 (*7*). Then,

$$n_o^* = (n_p + 1) + 3.14 - 0.24c_1 - 0.33c_2 - 0.16c_3 - 0.08c_4$$

$$n_o^* = 4.78 + 3.14 - (0.24 \times 2) - (0.33 \times 2) = 6.78$$

By the combining use of Equations 20 to 36 and the nomograms, the normal boiling point of the homologous compounds of 14 monosubstituted alkanes can be estimated. Except for some types of compounds mentioned below, the average deviation of estimation is lower than ±1.5° C. for more than 300 compounds. In the cases of ethers, ketones and esters having one or two tertiary α-carbon to the substituent, n_o^* is always underestimated, probably owing to the steric effect between the methyl sidechains. For example, the estimated normal boiling point of ethyl *tert*-butyl ether, *tert*-butyl formate, or *di-tert*-amylketone is 5° to 20° lower than the observed. The results and discussion of the present method will be described elsewhere in detail (*8*).

Variation of s in Mono-substituted Alkane Homologs. According to Equation 19, s can be determined from the vaporization entropy, $\Delta S°$. However, the precise estimation of difference in $\Delta S°$ from that of the reference alkane is not always easily performed, and it is desirable to find an empirical relationship on the structural variation of the s value in each homologous series.

As illustrated in Figures 11 to 13, a systematic variation is observed for each series, if s is plotted against n_o^*. These figures show that, except for the aliphatic acid series, the s *vs.* n_o^* relationship has a common character and that s is a small negative value in the lower range of n_o^* and converges monotonically to zero as n_o^* becomes large. On the other hand, s *vs.* n_o^* for the aliphatic acid series has a minimum value at an intermediate region of n_o^*. These facts may be interpreted as follows: In the case of monosubstituted alkanes, the contribution of a substituent decreases with increasing n_o^*, and there should be negligible difference in physical properties between parent and substituted hydrocarbons. The anomalous behavior of the acid series is due to the fact that in lower members such as formic or acetic acid, association of the molecules continues even in the vapor phase, and the molecule behaves as if it is nonpolar.

In most cases considered, the s *vs.* n_o^* relationship is well-established. Though an analytical expression has not been given, s *vs.* n_o^* curve may serve as a reference curve in graphical estimation.

APPENDIX

After the publication of the previous report (*9*), we have obtained the API RP 44 data sheets (*1*) which contain new selected values of T_b, $\Lambda°$, and $\Delta S°$, for normal paraffins. Furthermore, there were serious inconsistencies between the coefficients of the vapor pressure equations [Equations 13 to 25 in (*9*)]. These situations led us to re-determine the coefficients, as briefly described below.

First, the coefficients of Equation 13b in our previous paper (*9*) is determined from the normal boiling point data of propane to *n*-eicosane by the method of least squares, with the result that

$$\frac{n^{2/3}}{T_b} = \frac{B}{D} + \frac{C}{D}\,n^{2/3} = 0.0078237 + 0.00055431\,n^{2/3} \qquad (A1)$$

From Equation A1,

$$C/B = 0.07085 \qquad (A2)$$

Next, D is calculated by the following equation

$$D = \left[\frac{\Lambda°}{Rn^{2/3}}\left(1 + \frac{C}{B}\,n^{2/3}\right) - \frac{D}{B}\right] \Big/ \left(1 + \frac{C}{B}\,n^{2/3}\right) \qquad (A3)$$

By comparing with the $\Lambda°$ values for ethane to *n*-dodecane, it is found that $D = 944°$ and, accordingly, $B = 7.386$ and $C = 0.5233$, respectively.

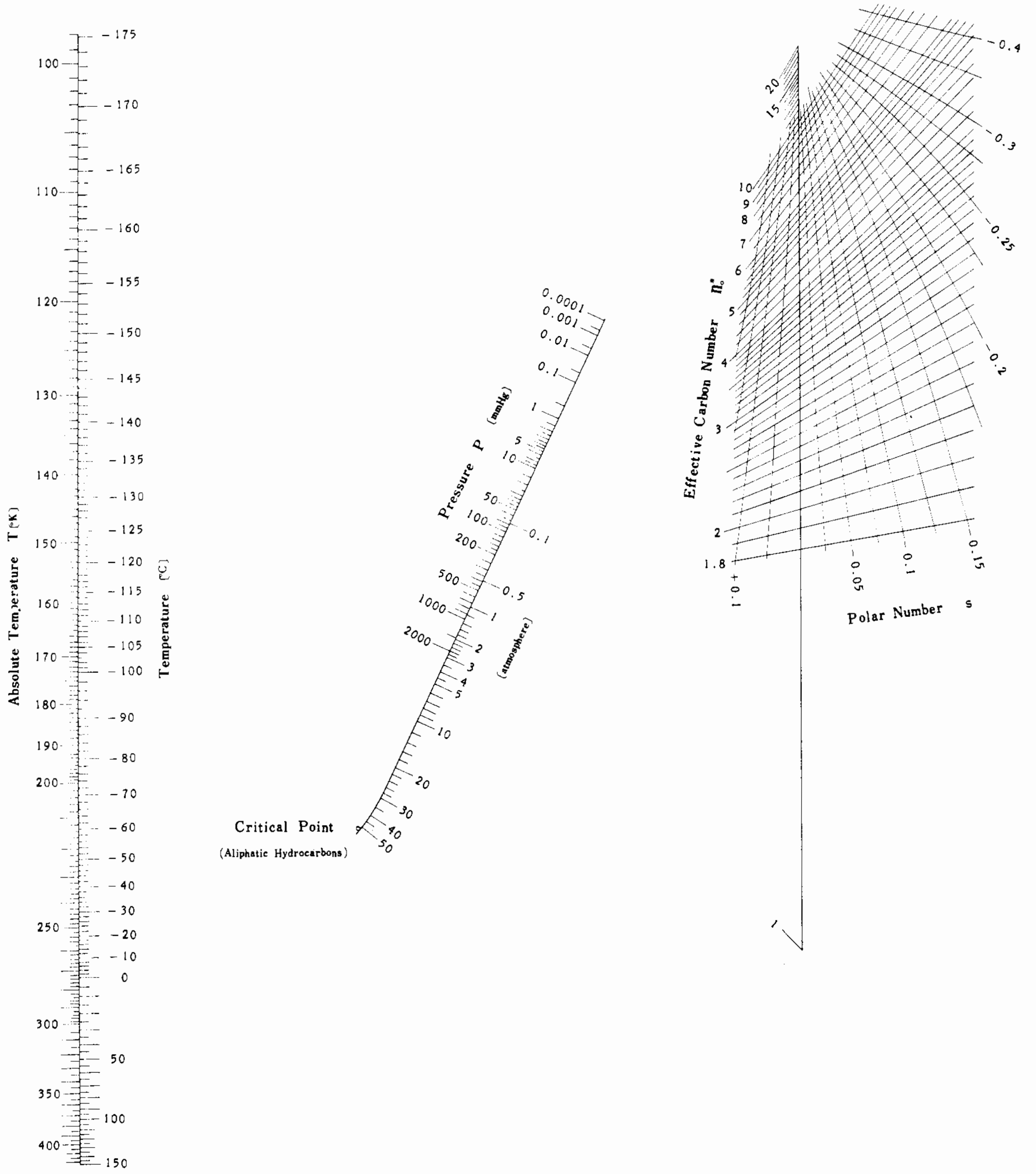

Figure 11. *s* vs. n_o^* relationship in monosubstituted alkane homologs (*1*) R- and R′- are alkyl groups and *n*-R-, normal alkyl group: closed marks are RX

β_1, β_2, and γ_1 in Equation 21 (*9*) are related to *B*, *C* and *D* by the following equations:

$$\beta_1 = (1 - B)/BD \tag{A4}$$

$$\beta_2 = 1/2DB^2 \tag{A5}$$

$$\gamma_1 = -C/DB^2 \tag{A6}$$

Using the value of *B*, *C*, and *D* estimated above and converting from ln *P* to log *P*, Equation 2 in the present text is obtained. The derivation that follows is the same as the previous one (*9*). The reproducibility of data by the revised equations is also comparable with the previous ones. Our present nomograms (Figures 4 to 7) are constructed on the basis of the previous equations. Since some empirical corrections have been made, the revision of coefficients in the basic equations has little effect on the scales of nomograms.

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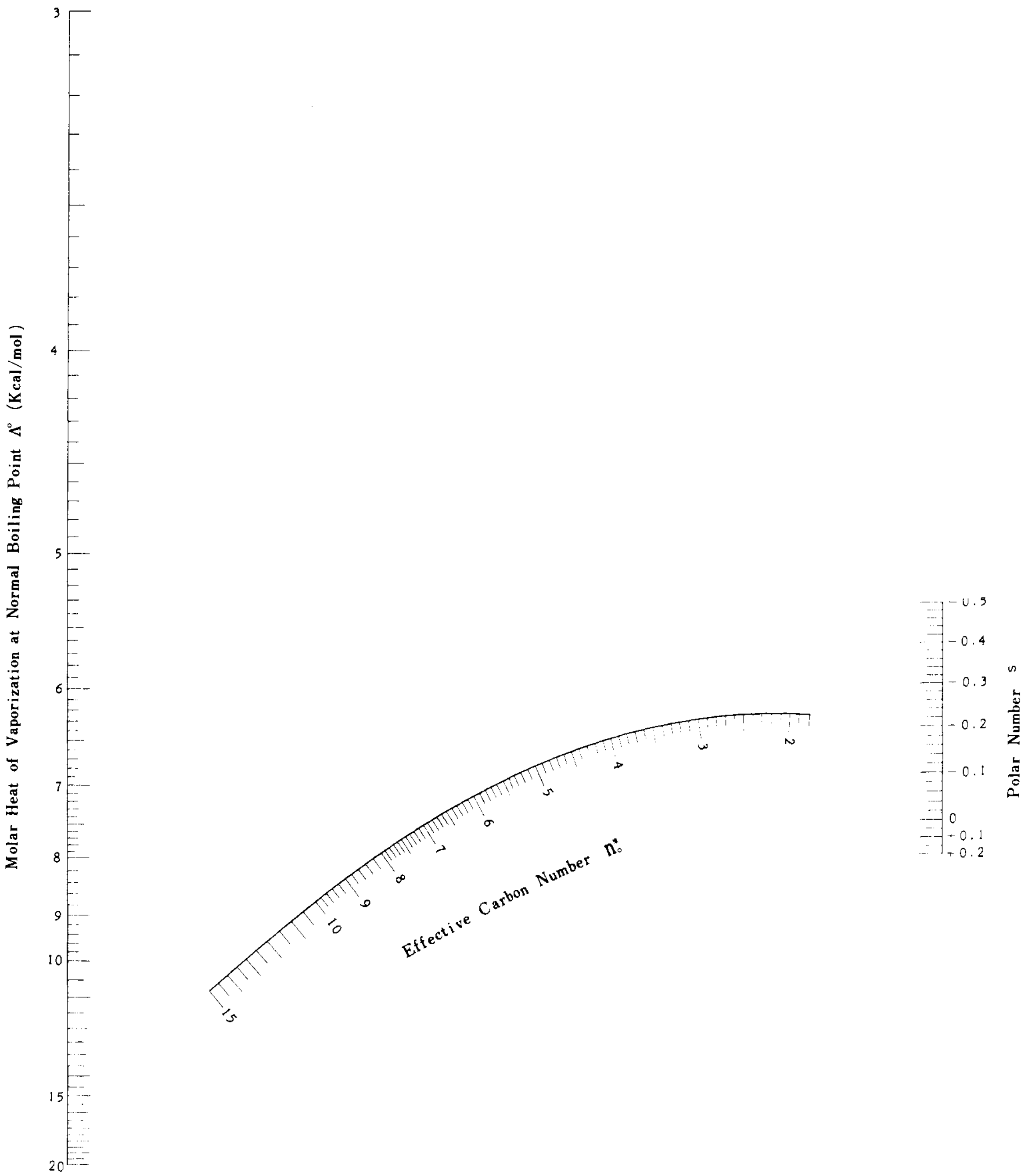

Figure 12. s vs. n_o^* relationship in mono-substituted alkane homologs (2)

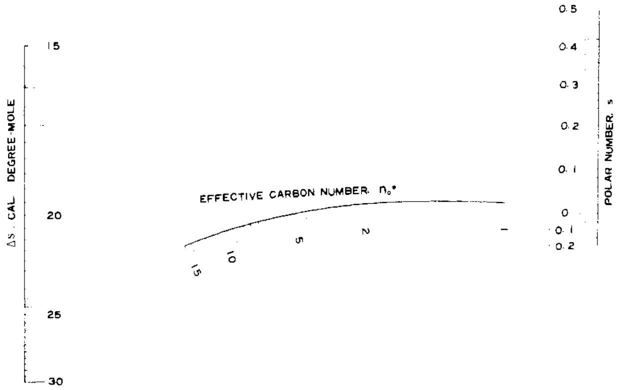

Figure 13. s vs. n_o^* relationship in mono-substituted alkane homologs (3)

NOMENCLATURE

A', B', C', D', E', = constants in the vapor pressure equation
B, C, D = constants in appendix
c_1, c_2, c_3, c_4 = constants in n_o^* equation
α, α- β, = points for extrapolation of n_o^* values
$\beta_1, \beta_2, \gamma_1$ = corrected values for B, C, D
f, g, h, = constants in the heat of vaporization calculation
n = number of carbon atoms
n^* = effective carbon number
n_o^* = effective carbon number at normal boiling point
n_p = carbon number or effective carbon number of parent paraffin
P = pressure, mm. of Hg
R = gas constant
s = polar number

ΔS° = entropy of vaporization at normal boiling point, cal./° C. mole

ΔS_p° = ΔS° for the corresponding normal paraffin having $n = n_o^*$

T = temperature, ° C.

T_b = boiling point, ° C.

T_b° = normal boiling point, ° C.

t = constant in Equation 15

λ = heat of vaporization, kcal./mole

λ° = heat of vaporization at normal boiling point, kcal./mole

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Cryoscopic Investigations and Phase Equilibria

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Partial phase diagrams have been determined for the $NaNO_3$–$NaCl$, $NaNO_3$–$Ba(NO_3)_2$, $NaNO_3$–Na_2MoO_4, and KNO_3–KCl systems by means of cooling curves and direct solubility determinations, and eutectic temperatures and compositions are reported. Freezing point depressions for dilute solutions of various salts in $NaNO_3$ and KNO_3 have been measured differentially and used to calculate heats of fusion.

WE HAVE determined partial phase diagrams for the $NaNO_3$-$NaCl$, $NaNO_3$-$Ba(NO_3)_2$, $NaNO_3$-Na_2MoO_4, and KNO_3-KCl systems and have made precise measurements of freezing point depressions in $NaNO_3$ and KNO_3 from which we have calculated heats of fusion. Phase diagrams have been deduced from cooling curves and direct solubility determinations. Freezing point depressions have been measured more precisely than is customary for investigations of dilute molten salt solutions.

EXPERIMENTAL

Chemicals. All chemicals were of C.P. grade and were dried by heating before they were used. $BaCl_2$ was obtained by dehydration of $BaCl_2 \cdot 2H_2O$ at about 120° C. until weight was constant.

Apparatus and Procedure. A cylindrical aluminum block surrounded by Kaylo insulation in a chemical drum has been used as a furnace. Holes were drilled in the aluminum block to accommodate two borosilicate glass sample tubes and one junction of a thermocouple. Other holes were drilled in the block and slots were milled around the circumference of the block to accommodate Nichrome heaters.

For cooling curve experiments one of the test tubes in the block was charged with a 40-gram sample of the desired composition. The sample and block were heated by the block heaters to 25° C. above the liquidus temperature and maintained at this temperature for several minutes. Then the block and sample were allowed to cool at a rate of about 0.8° per minute.

The sample tube contained a 5-mm. borosilicate glass tube to protect two Chromel-Alumel thermocouple junctions. One of these junctions was connected to a reference junction at 0° C. and gave the temperature of the sample. The other junction in the sample was connected to a reference junction in a hole in the block, as suggested by Beusman (*1*). A helical glass stirrer in the test tube was moved up and down over a 2-inch stroke at a rate of 57 strokes per minute by a motor. An aluminum cap with holes for the thermocouple tube and stirrer fitted over the top of the sample tube.

One thermocouple was calibrated at the boiling point of water and the freezing points of lead, tin, and zinc with the recorder later used for recording cooling curves.

Because of difficulty in detecting the change in slope of the cooling curve that corresponds to the liquidus temperature, we also recorded the output of the thermocouple with its reference junction in the block. When the liquidus temperature was reached, the output of this thermocouple increased sharply, and clearly indicated the time corresponding to the liquidus temperature on the cooling curve. Liquidus temperatures were determined in this way to ±0.5°. Eutectic temperatures were obtained directly from the cooling curves to ±0.5°.

When experiments like those described above are carried out separately on solutions and on the pure major component of the solutions, freezing point depressions are calculated as the difference in liquidus temperatures. We have used another procedure that is better for such investigations of dilute solutions. One tube in our apparatus was loaded with the pure major component and the other with a mixture of the desired composition. After both samples were completely melted and in equilibrium with the block, the block was allowed to cool at a rate of about