*Studies on Azeotropic Mixtures. II. Constancy of Molecular Interchange Energies in Homologous Azeotropic Series and Calculation of Azeotrope-forming Range**

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Introduction

Reflecting the importance of azeotrope formation in the distillation process, a great number of experimental data have been accumulated in recent times[1]. Also, several independent correlation rules of azeotropic data have been proposed on the practical side[2]. They are, however, all empirical and it appears difficult to find out the physical basis from any of them or to derive the one from the other without any additional assumptions. The following is an attempt to correlate binarily azeotropic data by a method with explicit representation of interaction energies of component molecules.

Recently Prigogine[3] has presented a similar method of correlating azeotropic

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1) L. H. Horsley, "Azeotropic Data", American Chemical Society (1952); F. D. Rossini, B. J. Mair and A. J. Streiff, "Hydrocarbons from Petroleum", Reinhold (1952), p. 88; L.H. Horsley, *Anal. Chem.*, **19**, 508 (1947); **21** 831 (1949); Lange, "Handbook of Chemistry", 5th ed., Handbook Publishers (1944); Ewell, Harrison and Berg, *Petroleum Engr.*, **16** 219, 255, 259 (1944); "Chemical Engineers' Handbook" 2nd ed., McGraw-Hill (1941); "International Critical Tables" Vol.3 McGraw-Hill (1928); M. Lecat, "La tension de vapeur des mélanges des liquides. L'Azéotropisme", Lamertin, Brussels (1918).

2) M. Lecat, *Z. anorg. u. allgem. Chem.*, **186**, 123 (1930); H. Skolnik, *Ind. Eng. Chem.*, **40**, 442 (1948); H. P. Meissner and S. H. Greenfeld, ibid., **40**, 438 (1948); R. L. Denyer, F. A. Fidler and R. A. Lowry, ibid., **41**, 2727 (1949); D. H. Desty and F. A. Fidler, ibid., **43**, 905 (1951); L. H. Horsley, *Anal. Chem.*, **19**, 603 (1947).

3) I. Prigogine and R. Defay, "Chemical Thermodynamics", (Translated by D. H. Everett), Longmans (1954), Chapt. XXVIII.

data that is very satisfactory also from our standpoint. As has been mentioned in part I[4], our standpoint is, however, a little different from that of Prigogine in that we are always considering the phenomenon from the molecular point of view, i. e., using the explicit form of the molecular interchange energy.

Graphical Method of Correlating Azeotropic Data

It has been shown in part I[4] that the azeotrope-forming power of many binary solutions could be estimated by molecular interchange energies w which were calculated from

$$\Delta_v S_1^0(T_1^0-T^a)=Nwx_2^2 \quad (1)$$

and

$$\Delta_v S_2^0(T_2^0-T^a)=Nwx_1^2, \quad (2)$$

where T^a is the azeotropic point (for $p=$ 1 atm.), N the Avogadro number and $\Delta_v S_i^0$ the molar entropy of vaporization at boiling point (for $p=1$ atm.) of ith pure component. ($i=1$ and 2).

Here, w is expressed, based on the quasi-crystalline model of the solution, as

$$w=\frac{z}{2}(\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12}),$$

where z is the average coordination number of the quasi-lattice and ε's are all the absolute average potential energies of molecular pairs. Equations (1) and (2) have only one unknown parameter w, all others being known from experiment.

Trouton proposed the celebrated rule that the entropy of vaporization is the same for all liquids[5]. A glance at the entropies of vaporization (for $p=1$ atm.) given in literature[6] shows, however, that the rule applies only roughly, and departs seriously from the truth if the liquids are "abnormal". Nevertheless, the rule appears to stand, to some degree, for members of homologous series if the liquids are not so highly associated. This condition will accordingly make it possible to apply invariably the equations (1) and (2) to the azeotropes formed by a fixed azeotropic reagent (or azeotrope former) with a series of homologues, if w_s are nearly the same for the series of azeotropes. Thus, if these allowances are made, we can expect straight-line relationships between $T_i^0-T^a$ and x_i^2 for the series.

In the following, we have examined the relationship on a number of series by taking the known values of the thermodynamic quantities appearing in equations (1) and (2). In most cases, however, because of lack of data, an appropriate value of $\Delta_v S_1^0$ for the series is assumed from the known values for a few members of the series.

In each case two kinds of plots, that is, first $T_2^0-T^a$ against x_1^2 and second $T_1^0-T^a$ against x_2^0 are presented. For each case the second component 2 is a fixed azeotropic reagent and the first components 1 are homologous members. Examples taken are arranged into four classes according to the different types of intermolecular forces as in part I.

(a) Dispersion Force Solutions

Examples taken are azeotropes of toluene with paraffinic and naphthenic hydrocarbons. They form always minimum type azeotropes[4] (A, Fig. 1).

(b) Solutions Involving Addition Compounds

Examples taken are azeotropes of bromodichloromethane with "donor type" liquids such as ketones and esters. They form always maximum type azeotropes[4] (B, Fig. 2).

(c) Solutions Involving Associations in Non-polar Solvents

This class involves most of the useful azeotropes, since they have the largest azeotrope-forming powers among four classes. The following nine series are taken as examples.

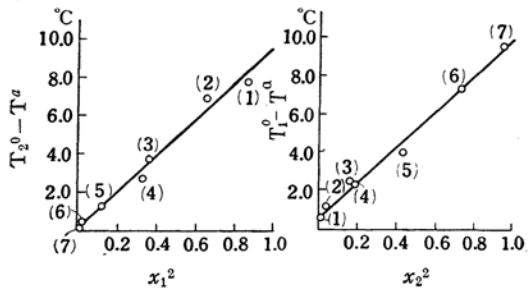

Fig. 1. The plots of toluene azeotropes with aliphatic hydrocarbons.
Aliphatic hydrocarbons (A): (1), ethylcyclopentane; (2), 1,1,3-trimethylcyclopentane; (3), 2,5-dimethylhexane; (4), *cis-trans-cis*-1,2,4-trimethylcyclopentane; (5), 2,3,4-trimethylpentane; (6), 2-methylheptane; (7), *cis*-1,3-dimethylcyclohexane.

4) T. Yoshimoto and Y. Mashiko, This Bulletin, **29**, 990 (1956).
5) F. Trouton, *Phil. Mag.* (5), **18**, 54 (1884).
6) "International Critical Table", Vol. V (1929).

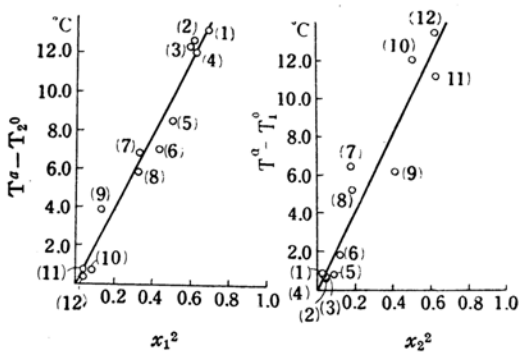

Fig. 2. The plots of bromodichloromethane azeotropes with "donor type liquids".
Donor liquids (B): (1), methyl butyrate; (2), 2-pentanone; (3), 3-pentanone; (4), propyl acetate; (5), isobutyl formate; (6), 3-methyl-2-butanone; (7), *n*-propyl ether; (8), isopropyl acetate; (9), diethoxymethane; (10), propyl formate; (11), 2-butanone; (12), ethyl acetate.

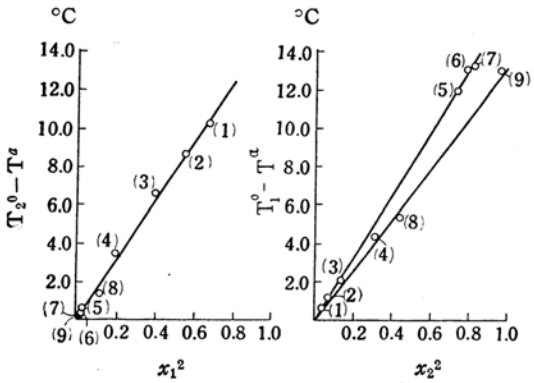

Fig. 3. The plots of 1-propanethiol azeotropes with paraffinic and naphthenic hydrocarbons.
Paraffinic hydrocarbons (C): (1), 2,3-dimethylbutane; (2), 2-methylpentane; (3), 3-methylpentane; (4), *n*-hexane; (5), 2,2-dimethylpentane; (6), 2,4-dimethylpentane; (7), 2,2,3-trimethylbutane.
Naphthenic hydrocarbons(D): (8), methylcyclopentane; (9), cyclohexane.

1-Propanethiol
—Paraffinic Hydrocarbons (C, Fig. 3)
1-Propanethiol
—Naphthenic Hydrocarbons (D, Fig. 3)
1-Butanethiol
—Paraffinic Hydrocarbons (E, Fig. 4)
1-Butanethiol
—Naphthenic Hydrocarbons (F, Fig. 4)
1,2-Benzenediol
—Aromatic Hydrocarbons (G, Fig. 5)
1,3-Benzenediol
—Aromatic Hydrocarbons (H, Fig. 6)

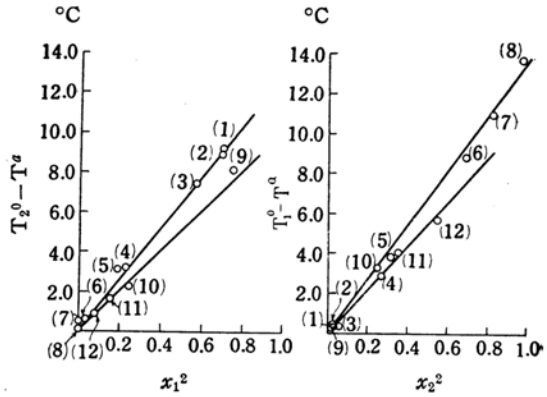

Fig. 4. The plots of 1-butanethiol azeotropes with paraffinic and naphthenic hydrocarbons.
Paraffinic hydrocarbons (E): (1), 2,3-dimethylpentane; (2), 2-methylhexane; (3), 3-methylhexane; (4), *n*-heptane; (5), 2,2,4-trimethylpentane; (6), 2,2-dimethylhexane; (7), 2,5-dimethylhexane; (8), 3,3-dimethylhexane.
Naphthenic hydrocarbones (F): (9), *trans*-1,3-dimethylcyclopentane; (10), *cis*-1,2-dimethylcyclopentane; (11), methylcyclohexane; (12), ethylcyclopentane.

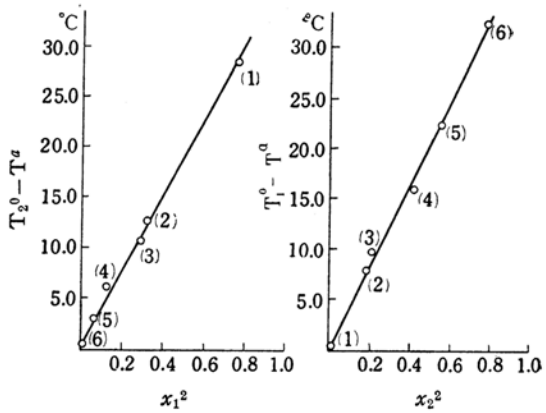

Fig. 5. The plots of 1,2-benzenediol azeotropes with aromatic hydrocarbons.
Aromatic hydrocarbons (G): (1), naphthalene; (2), 2-methylnaphthalene; (3), 1-methylnaphthalene; (4), biphenyl; (5), diphenyl methane, (6), acenaphthene.

Nitromethane
—Aliphatic Hydrocarbons (I, Fig. 7)
Nitromethane
—Aromatic Hydrocarbons (J, Fig. 7)
Methanol
—Paraffinic Hydrocarbons (K, Fig. 8)

The last involves highly associated liquid that is apparently not to be regarded as a component of regular solutions even at azeotropic points[4].

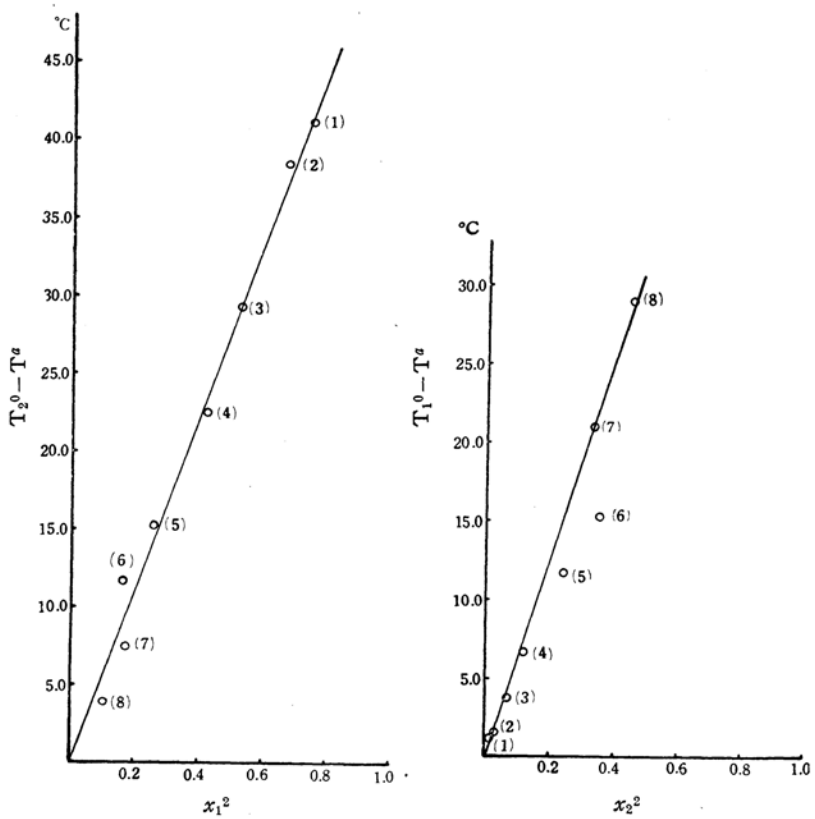

Fig. 6. The plots of 1,3-benzenediol azeotropes with aromatic hydrocarbons.
Aromatic hydrocarbons (H): (1), 2-methylnaphthalene; (2), 1-methylnaphthalene; (3), biphenyl; (4), diphenyl methane; (5), acenaphthene; (6), 1,2-diphenylethane; (7), fluorene; (8), *trans*-stilbene.

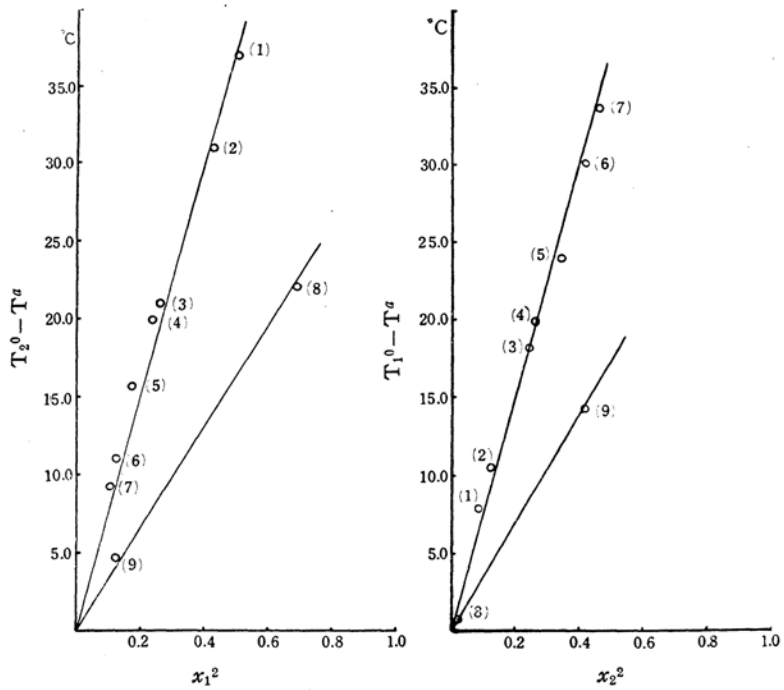

Fig. 7. The plots of nitromethane azeotropes with aliphatic and aromatic hydrocarbons.
Aliphatic hydrocarbons (I): (1), methylcyclopentane; (2), cyclohexane; (3), *n*-heptane; (4), methylcyclohexane; (5), 2,5-dimethylhexane; (6), 1,3-dimethylcyclohexane; (7), *n*-octane. Aromatic hydrocarbons (J): (8), benzene; (9), toluene.

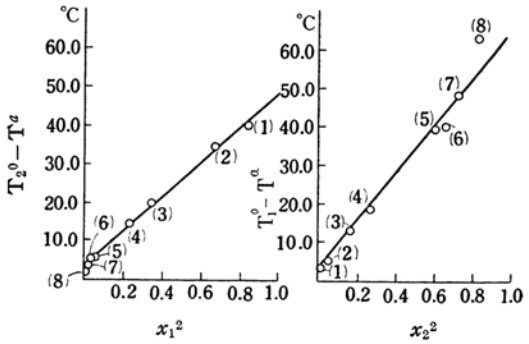

Fig. 8. The plots of methanol azeotropes with paraffinic hydrocarbons.
Paraffinic hydrocarbons (K): (1), isopentane; (2), *n*-pentane; (3), 2,3-dimethylbutane; (4), *n*-hexane; (5), *n*-heptane; (6), 2,2,4-trimethylpentane; (7), 2,5-dimethylhexane; (8), *n*-octane.

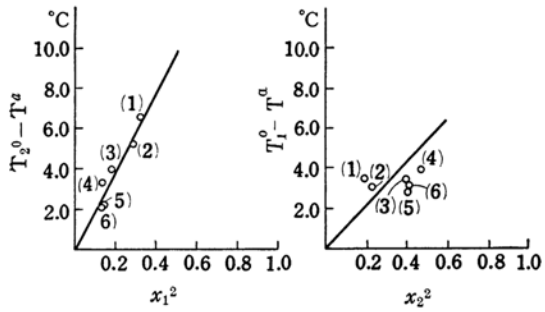

Fig. 9. The plots of nitromethane azeotropes with ketones and esters.
Ketones and esters (L): (1), butyl formate; (2), ethyl propionate; (3), propyl acetate; (4), methyl butyrate; (5), 3-pentanone; (6), 2-pentanone.

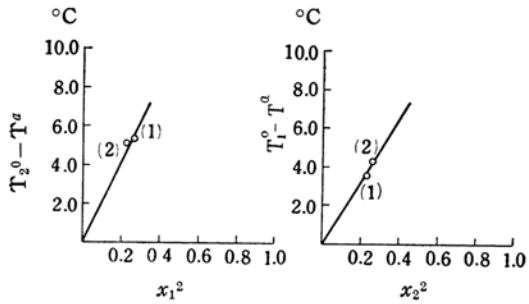

Fig. 10. The plots of acetonitrile azeotropes with esters.
Esters (M): (1), methyl propionate; (2), propyl formate.

(d) Solutions Involving Associations in Polar Solvents

Azeotropes in this class have smaller azeotrope-forming powers and involve more complicated interaction of component molecules than those in class (c).

Examples taken are as follows.
Nitromethane
—Ketones and Esters (L, Fig. 9)
Acetonitrile—Esters (M, Fig. 10)

In general the straight-line relationship is observed satisfactorily in every plot except the series which involves special molecular interactions such as in class (b) and (d). Furthermore, as shown in Table I, the slopes of two independent plots that involve $T_1^0 - T^a$ and x_2^2 on the one hand, and $T_2^0 - T^a$ and x_1^2 on the other are approximately equal when devided by $\Delta_v S_1^0$ and $\Delta_v S_2^0$ respectively. This leads to a conclusion from equations (1) and (2) that the molecular interchange energy w of azeotropes, which are formed between a fixed azeotropic reagent and members of a homologous series, is characteristic of the series in many cases and therefore regarded as azeotrope-forming power of a series of azeotropic mixtures. The new correlation thus introduced from equations (1) and (2) is considered to be essential to compare azeotrope-forming powers of a number of solutions.

TABLE I

MOLECULAR INTERCHANGE ENERGIES CALCULATED FROM THE SLOPES OF TWO KINDS OF PLOTS

Azeotropic[a] Series	$N\omega_1$ $\left(\frac{\text{kcal.}}{\text{M}}\right)$	$N\omega_2$ $\left(\frac{\text{kcal.}}{\text{M}}\right)$	$\Delta_v S_1^{0}$[b] $\left(\frac{\text{cal.}}{\text{M°C}}\right)$	$\Delta_v S_2^{0}$[b] $\left(\frac{\text{cal.}}{\text{M°C}}\right)$
A	190	200	(20.3)	20.8
B	−450	−430	(22.0)	21.0
C	340	340	(20.3)	(22.0)
D	270	—	(20.4)	—
E	280	280	(20.3)	(22.0)
F	230	230	(20.3)	(22.0)
G	850	850	(20.3)	(22.5)
H	1300	1300	(20.3)	(23.5)
I	1560	1630	(20.3)	22.1
J	710	730	20.8	22.1
K	1170	1140	(20.3)	25.0
L	Diffuse	420	—	22.1
M	360	420	(22.0)	20.2

a) Azeotropic data are all taken from Horsley's "Azeotropic Data"[1].
b) Values taken from "International Critical Table" Vol. V (1929). Values enclosed in parentheses are assumed ones.

Here, it should be mentioned from the view-point of our approximation[4] that as x_2 approaches to 0 in $(T_1^0 - T^a) - x_2^2$ plots and x_1 to 0 in $(T_2^0 - T^a) - x_1^2$ plots, the error of the above approximation will be considerable. In fact, the error in the plots of methanol-paraffins series is remarkable as shown in Fig. 8, while it is con-

sidered to be small in other series according to the results so far obtained. The $(T_1^0-T^a)-x_2^2$ plots in toluene-hydrocarbons series does not pass through the origin (Fig. 1). The cause of this abnormality is uncertain and will be left to the further study.

Azeotrope-forming Range

From equations (1) and (2) we obtain maximum boiling point $T_1^{0\max}$ and minimum boiling point $T_1^{0\min}$ of pure component 1 that can form azeotropes with component 2 as follows.

If $w>0$, we have

$$T_1^{0\max}=T_2^0+\frac{Nw}{\Delta_v S_1^0} \tag{3}$$

and

$$T_1^{0\min}=T_2^0-\frac{Nw}{\Delta_v S_2^0}. \tag{4}$$

If $w<0$, we have

$$T_1^{0\max}=T_2^0+\frac{Nw}{\Delta_v S_2^0} \tag{5}$$

and

$$T_1^{0\min}=T_2^0-\frac{Nw}{\Delta_v S_1^0}. \tag{6}$$

Graphically the intercepts of the lines with the ordinate at $x_2^2=1$ in $(T_1^0-T^a)-x_2^2$ plots and at $x_1^2=1$ in $(T_2^0-T^a)-x_1^2$ plots give respectively $T_1^{0\max}$ and $T_1^{0\min}$ (see Figs. 1–10). The difference between maximum and minimum boiling points give therefore the boiling point range, over which azeotrope formation is allowable for the series. Denyer et al.[7] and Swietoslawsky[8] regarded azeotrope-forming range, $T_1^{0\max}-T_1^{0\min}$, as a measure of the azeotrope-forming powers of a given azeotropic series. We have for this range, with explicit representation of w, from (3) and (4) or (5) and (6),

$$T_1^{0\max}-T_1^{0\min}=Nw\left(\frac{1}{\Delta_v S_1^0}+\frac{1}{\Delta_v S_2^0}\right). \tag{7}$$

$T_1^{0\max}$ and $T_1^{0\min}$ are calculated from w's which are obtained from the slopes of plots in Figs. 3 and 4, and are presented in Table II along with those obtained from Denyer's and Skolnik's[9] plots. The agreement is excellent. Denyer's and Skolnik's azeotropic ranges are considered to be slightly different in their physical meaning, though the difference will be trivial whenever w is small as will be shown later.

TABLE II

COMPARISON OF T_1^0 max AND T_1^0 min CALCULATED BY THREE METHODS

Azeotropic Series	This work		Denyer's		Skolnik's
	T_1^0 max (°C)	T_1^0 min (°C)	T_1^0 max (°C)	T_1^0 min (°C)	T_1^0 max (°C)
C	85	52	84	52	83.5
E	112	86	112	85	112

Conclusion

Applying Trouton's rule to a homologous series, the constancy of molecular interchange energy w for azeotropes composed of a fixed component and the series is exemplified in a number of cases. The fundamental equations derived in part I is thus proved to be useful in correlating azeotropic data. Also maximum and minimum boiling points of components in a homologous azeotropic series are derived and values calculated are compared with those obtained by other methods.

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7) R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind Eng. Chem.*, **41**, 2727 (1949); D. H. Desty and F. A. Fidler, ibid., **43**, 905 (1951).

8) W. Swietoslawsky, *Prezemyl. Chem.*, **1**, 363 (1951).

9) H. Skolnik, *Ind. Eng. Chem.*, **40**, 442(1948).