

INTRODUCTION OF THE REDUCED SURFACE
ENERGIES AT ZERO ABSOLUTE TEMPERATURE

by

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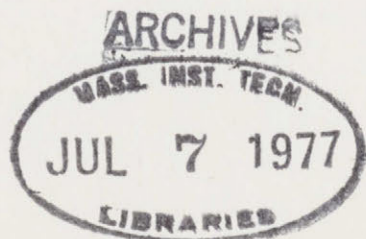
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on February 1977 in partial fulfillment of the requirements
for the degree of Bachelor of Science.

ABSTRACT

A new group of dimensionless parameteres, "the reduced surface energies at zero absolute temperature", for pure normal fluid substances is introduced.

A method is developed and demonstrated to calculate the values of these parameters for six different pure normal fluid substances.

The resulting reduced surface energies for the different fluids investigated is remarkably constant.

Thesis Spervisor: Professor Henry M. Paynter

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This thesis could never have been done without the original ideas of Professor Henry M. Paynter who fully supervised this work through the entire stages of completion.

Table of contents

Abstract.....	2
List of Tables.....	5
1. Introduction.....	6
2. Historical background.....	8
3. The reduced zero-point energies.....	10
4. Calculation of zero-point energy.....	12
5. Results and discussion.....	15
6. Recommendations.....	17
Table 1.....	18
Table 2.....	19
Table 3.....	20
Table 4.....	21
Table 5.....	22
Table 6.....	23
Table 7.....	24
Table 8.....	25
Table 9.....	26
Table 10.....	27
Figure 1.....	29
Nomenclature.....	30
References.....	31
Appendix A.....	32
Appendix B.....	34

List of Tables

Table 1 : Critical properties of the investigated fluids.....18

Table 2 : Zero-point energies of the investigated fluids " Macleod's data".....19

Table 3 : Zero-point energies of the investigated fluids " Sugden's data".....20

Table 4 : First order parameteres "Macleod's data".....21

Table 5 : Arithmetic mean parameteres "Macleod's data"..22

Table 6 : Geometric mean parameteres "Macleod's data"..23

Table 7 : First order prameteres "Sugden's data".....24

Table 8 : Arithmetic mean parameteres "Sugden's data"..25

Table 9 : Geometric mean parameteres "Sugden's data"...26

Table 10: Calculated values of surface tension for several fluids using Eq.2627

Figure 1: Comparison between calculated values of surface tension and published values of surface tension.....29

1. Introduction

Values of surface energies at zero absolute temperature, "zero-point energy", were extrapolated from experimental values of surface tension for six pure normal fluid substances, taken from papers of Macleod (1), and Sugden (2)*.

The method of "least-squares" was employed to find the proper exponent, μ , and zero-point energy, E_0 , for the fluids investigated, assuming a general formula of the form

$$\sigma = \sigma_0 (1 - T/T_c)^\mu \quad (1)$$

relating surface tension and temperature.

Dimensionless groups of zero-point energies were formed using critical properties of fluids and surface energy at zero absolute temperature. The dimensionless groups of zero-point energies are remarkably constant for the fluids investigated.

Values of surface tension for several fluids were calculated, and compared to their published values, using one of the dimensionless parameteres, namely

$$\epsilon_{13g} = E_0 / [P_c^{1/3} T_c^{5/12} (\rho_c g_0)^{1/4}]$$

* Macleod's data (1) were taken from the paper of Ramsay-Shields (3) which was published in German. Sugden's data (2) were taken from the paper of Ramsay-Shields (4) which was

The results of this comparison are illustrated in Table 10 and Fig.1 .

published in English. Sugden corrected the data given by Ramsay and Shields which he believed were not accurate due to an inadequate correction for the capillary rise in the wider tube.

2. Historical background

In 1886, Eötvös (5) deduced an equation for the variation of surface tension with temperature from consideration of "corresponding states" of liquids of similar molecular consideration, in the form of:

$$-d[\sigma(M\nu)^{2/3}]/dT=k \quad (2)$$

where k is called Eötvös constant.

Integration of Eq.2 gives the following equation:

$$\sigma(M\nu)^{2/3} = k(T_c - T) \quad (3)$$

Noticing that surface tension vanishes as temperature approaches the critical temperature.

Ramsay and Shields (4) modified the equation of Eötvös, taking into consideration the nonlinear behaviour of surface tension at neighbourhood of the critical point. They suggested the following formula:

$$\sigma(M\nu)^{2/3} = k(T_c - T - \delta) \quad (4)$$

van der Waals (6) deduced relations between surface tension and temperature for the liquids complying with the law of corresponding states.

$$\sigma = K_1 \left(\frac{T_c}{T} \right)^{-2/3} \nu_c^B (1 - T/T_c) \quad (5)$$

$$\sigma = K_2 \left(\frac{T_c}{T} \right)^{1/3} \left(\frac{P_c}{P} \right)^{2/3} (1 - T/T_c)^B \quad (6)$$

where K_1 , K_2 , and B are universal constants.

Katayama (7) modified the equation of Eötvös for the effect of vapor pressure above the liquid surface, and proposed the equation:

$$\sigma [M/(\rho_l - \rho_v)]^{2/3} = k T_c (1 - T/T_c) \quad (7)$$

Guggenheim (8) employed Katayama's relation to the liquids complying to the law of corresponding states and deduced the following equation:

$$\sigma = \sigma_0 (1 - T/T_c)^{11/9} \quad (8)$$

Guggenheim showed that Eq.6 and Eq.7 were mutually interdependent.

van der Waals' formula, Eq.5 and Eq.6, reduce to that of Guggenheim-Katayama if B is given the value of $11/9$, and σ_0 is equated to $K_1 T_c \nu_c^{-2/3}$, or to $K_2 T_c^{1/3} P_c^{2/3}$. van der Waals derived the $K_1 T_c \nu_c^{-2/3}$ term, and $K_2 T_c^{1/3} P_c^{2/3}$ term by means of dimensional analysis. He carried out the calculation by using only two critical constants at a time.

3. The reduced zero-point energies

The critical constants P_c , T_c , and ρ_c were used to scale the zero-point energy. Employing only two of the critical constants at a time, the following dimensionless parameters were formed:

$$\epsilon_1 = E_o / (P_c^{2/3} T_c^{1/3}) \quad (9)$$

$$\epsilon_2 = E_o / [P_c^2 (\rho_c g_o)^{-1}] \quad (10)$$

$$\epsilon_3 = E_o / [T_c^{1/2} (\rho_c g_o)^{1/2}]. \quad (11)$$

Additional parameters were followed by forming the arithmetic means, and geometric means of the above parameters:

$$\epsilon_{ij\alpha} = (\epsilon_i + \epsilon_j) / 2 \quad (12)$$

$$\epsilon_{ijg} = (\epsilon_i \epsilon_j)^{1/2} \quad (13)$$

and

$$\epsilon_{123\alpha} = (\epsilon_1 + \epsilon_2 + \epsilon_3) / 3 \quad (14)$$

$$\epsilon_{123g} = (\epsilon_1 \epsilon_2 \epsilon_3)^{1/3}. \quad (15)$$

Therefore, a sequence of 11 parameters were formed for the six fluids investigated, using the computed values of zero-point energies*, and published critical values (9).

* See section 4.

Below, the 4 geometric mean parameteres are shown in the calculated form:

$$\epsilon_{12g} = E_o / [Pc^{4/3} Tc^{1/6} (\rho_c g_o)^{-1/2}] \quad (16)$$

$$\epsilon_{13g} = E_o / [Pc^{1/3} Tc^{5/12} (\rho_c g_o)^{1/4}] \quad (17)$$

$$\epsilon_{23g} = E_o / [Pc^{1/4} Tc^{-1/4} (\rho_c g_o)] \quad (18)$$

$$\epsilon_{123g} = E_o / [Pc^{8/9} Tc^{5/18} (\rho_c g_o)^{-1/6}]. \quad (19)$$

4. Calculation of zero-point energy

The general equation relating surface tension to temperature could be written as:

$$\sigma = \sigma_0 (1 - T/T_c)^\mu, \quad (20)$$

assuming the exponent, μ , is not constant for different fluid substances.

Equation 20 was substituted in the general thermodynamics relationship between total surface energy, E_σ , and free surface energy, σ ,

$$E_\sigma = \sigma - T d\sigma/dT, \quad (21)$$

to develop an equation for the variation of total surface energy with temperature. Total surface energy equation becomes:

$$E_\sigma = \sigma_0 [1 + (\mu - 1) T/T_c] (1 - T/T_c)^{\mu - 1} \quad (22)$$

Equations 20, and 22 show that total surface energy at zero absolute temperature, "zero-point energy", has in fact the same magnitude as surface tension at zero absolute temperature. In other words,

$$E_0 = \sigma_0 \quad (23)$$

Total surface energy stays almost constant for a wide range of temperature near the absolute zero temperature. Therefore, a more stable value could be calculated for zero-

point energy than zero-point surface tension.

The total surface energies at various temperatures for the fluids investigated were extrapolated from the surface tension data, employing the method of numerical differentiation*.

Equation 21 was used to carry out the calculations. In order to evaluate the values of zero-point energies, the calculated values of the total surface energies, and the proper values of exponent, μ , were substituted in Eq.22. A sample calculation of zero-point energy, E_0 , for Ethyl acetate is presented in Appendix B.

The calculated value of zero-point energy, E_0 , should be, for each investigated fluid substances, independent of the various values of the total surface energy at different temperatures. The method of "least-squares" was employed to find the proper value of the exponent, μ , in order of stabilize the value of zero-point energy, E_0 . A straight line relationship was assumed for E_0 , and surface tension, σ , in the form of:

$$E_0 = a\sigma + b \quad (24)$$

As a first try, value of 1.22 was tried for μ , and it was varied by increments of ± 0.01 , until the slope, a , approached zero.

*See Appendix A.

As "a" approaches zero, "b" represents the average value of zero-point energy. This value of b was used in calculation of the reduced zero-point energies.

A sample calculation of "b" for Ethyl acetate is presented in Appendix B.

Tables 2, and 3 show the calculated values of zero-point energies, E_0 , and the exponents, μ , for the investigated fluids.

5. Results and discussion

The procedure for calculation of surface energy at zero absolute temperature is outlined in Appendix B.

Table 1 contains the published critical properties of the six pure normal fluid substances (9) used in calculations.

The calculated values of the dimensionless parameteres are shown in Tables 4 to 9 for the investigated fluids.

The average values of the geometric mean parameteres are:

$$\epsilon_{12g} = 2.73 \times 10^{-8}$$

$$\epsilon_{13g} = 3.20 \times 10^{-3}$$

$$\epsilon_{23g} = 1.33 \times 10^{-6}$$

$$\epsilon_{123g} = 4.87 \times 10^{-6}$$

ϵ_{13g} is the most stable amongst the dimensionless parameteres. In order to examine the validity of the basic concept, the average value of ϵ_{13g} was used to calculate the surface tension of several other fluids. The calculated values of surface tensions were then compared to the ones published (10).

Solving for E_o in Eq.17, and substituiting σ_o for E_o , the following equation is derived:

$$\sigma_o = \epsilon_{13g} P_c^{1/3} T_c^{5/12} (\rho_c g)^{1/4} \quad (25)$$

Substituiting Eq.25 in Eq.20 gives :

$$\sigma = E_{13g} P_c^{1/3} T_c^{5/12} (\rho_c g)^{1/4} (1-T/T_c)^{11/9} \quad (26)$$

Equation 26 was used to calculate the values of surface tension of several different fluids, taking the exponent, μ , to be 11/9. Table 10 and Fig.1 presents the results.

A study of Table 10 and Figure 1 shows that the calculated values of the surface tension are in the proximity of the published ones.

6. Recommendations

Other dimensionless groups of parameteres could be formed using the arithmetic weighted mean and geometric weighted mean of $\epsilon_1, \epsilon_2,$ and ϵ_3 in the following form:

$$\overline{\epsilon_{123a}} = \alpha_1 \epsilon_1 + \beta_1 \epsilon_2 + (1 - \alpha_1 - \beta_1) \epsilon_3 \quad (27)$$

where α_1 and β_1 are less than 1.

and,

$$\overline{\epsilon_{123g}} = \epsilon_1^{\alpha_2} \epsilon_2^{\beta_2} \epsilon_3^{(1 - \alpha_2 - \beta_2)} \quad (28)$$

or

$$\ln \overline{\epsilon_{123g}} = \alpha_2 \ln \epsilon_1 + \beta_2 \ln \epsilon_2 + (1 - \alpha_2 - \beta_2) \ln \epsilon_3 \quad (29)$$

where α_2 and β_2 are less than 1.

Depending on the choices of α_1 and β_1 , or of α_2 and β_2 , a more stable value for the parameteres might result, resulting in a more precise estimation of the surface tension for various fluids.

Table 1: Critical properties of the investigated fluids* .

Substance	Mol. wt.	Tc °K	Pc Atm.	Pc dyne/cm ²	v _c cm ³ /g mole	ρ _c g/cm ³
Benzene	78.11	562.1	48.6	4.93 x 10 ⁷	260	0.300
Carbon tetrachloride	153.84	556.4	45.0	4.56 x 10 ⁷	276	0.557
Chlorobenzene	112.56	632.4	44.6	4.52 x 10 ⁷	308	0.365
Diethyl ether	74.12	456.8	35.6	3.61 x 10 ⁷	274	0.271
Ethyl acetate	88.10	523.3	37.8	3.83 x 10 ⁷	286	0.308
Methyl formate	60.05	478.2	59.2	6.00 x 10 ⁷	172	0.349

* Data are taken from Ref.(9) .

Table 2: Zero-point energies of the investigated fluids;
using only Macleod's data.

Substance	μ	E_0 erg/cm ²
Benzene	1.19	66.54
Carbon tetrachloride	1.18	61.60
Chlorobenzene	1.23	68.70
Diethyl ether	1.22 [*]	55.20
Ethyl acetate	1.24	65.81
Methyl formate	1.22	76.25

* Due to insufficient data points, value of 1.22 was assumed for the exponent.

Table 3: Zero-point energies of the investigated fluids;
using only Sugden's data.

Substance	μ	E_0 erg/cm ²
Benzene	1.19	69.65
Carbon tetrachloride	1.16	64.72
Chlorobenzene	1.25	74.45
Diethyl ether	1.23	59.02
Ethyl acetate	1.24	67.47
Methyl formate	1.22	77.50

Table 4 : Reduced zero-point energies of the investigated fluids; using only Macleod's data.

First order parameteres

Substance	ϵ_1	ϵ_2	ϵ_3
Benzene	6.00×10^{-5}	8.07×10^{-12}	1.64×10^{-1}
Carbon tetrachloride	5.87×10^{-5}	1.62×10^{-11}	1.12×10^{-1}
Chlorobenzene	6.31×10^{-5}	1.20×10^{-11}	1.44×10^{-1}
Diethyl ether	6.52×10^{-5}	1.13×10^{-11}	1.57×10^{-1}
Ethyl acetate	7.18×10^{-5}	1.35×10^{-11}	1.65×10^{-1}
Methyl formate	6.32×10^{-5}	7.25×10^{-12}	1.87×10^{-1}

Table 5: Reduced zero-point energies of the investigated fluids; using only Macleod's data.

Arithmetic mean parameteres

Substance	ϵ_{12a}	ϵ_{13a}	ϵ_{23a}	ϵ_{123a}
Benzene	3.00×10^{-5}	8.18×10^{-1}	8.17×10^{-2}	5.45×10^{-2}
Carbon tetrachloride	2.93×10^{-5}	5.59×10^{-2}	5.59×10^{-2}	3.73×10^{-2}
Chlorobenzene	3.42×10^{-5}	7.83×10^{-2}	7.83×10^{-2}	5.22×10^{-2}
Diethyl ether	3.26×10^{-5}	7.85×10^{-2}	7.85×10^{-2}	5.23×10^{-2}
Ethyl acetate	3.59×10^{-5}	8.28×10^{-2}	8.27×10^{-2}	5.52×10^{-2}
Methyl formate	3.16×10^{-5}	9.34×10^{-2}	9.34×10^{-2}	6.23×10^{-2}

Table 6 : Reduced zero-point energies of the investigated fluids; using only Macleod's data.

Geometric mean parameteres

Substance	ϵ_{12g}	ϵ_{13g}	ϵ_{23g}	ϵ_{123g}
Benzene	2.20×10^{-8}	3.13×10^{-3}	1.15×10^{-6}	4.29×10^{-6}
Carbon tetrachloride	3.08×10^{-8}	2.560×10^{-3}	1.34×10^{-6}	4.74×10^{-6}
Chlorobenzene	2.75×10^{-8}	3.02×10^{-3}	1.32×10^{-6}	4.79×10^{-6}
Diethyl ether	2.71×10^{-8}	3.20×10^{-3}	1.32×10^{-6}	4.87×10^{-6}
Ethyl acetate	3.12×10^{-8}	3.45×10^{-3}	1.50×10^{-6}	5.44×10^{-6}
Methyl formate	2.14×10^{-8}	3.44×10^{-3}	1.16×10^{-6}	4.41×10^{-6}

Table 7 : Reduced zero-point energies of the investigated fluids; using only Sugden's data.

First order parameteres

Substance	ϵ_1	ϵ_2	ϵ_3
Benzene	6.28×10^{-5}	8.45×10^{-12}	1.71×10^{-1}
Carbon tetrachloride	6.16×10^{-5}	1.70×10^{-11}	1.17×10^{-1}
Chlorobenzene	6.83×10^{-5}	1.30×10^{-11}	1.56×10^{-1}
Diehyl ether	6.97×10^{-5}	1.20×10^{-11}	1.68×10^{-1}
Ethyl acetate	7.36×10^{-5}	1.39×10^{-11}	1.70×10^{-1}
Methyl formate	6.43×10^{-5}	7.37×10^{-12}	1.90×10^{-1}

Table 8 : Reduced zero-point energies of the investigated fluids; using only Sugden's data.

Arithmetic mean parameteres

Substance	ϵ_{12a}	ϵ_{13a}	ϵ_{23a}	ϵ_{123a}
Benzene	3.14×10^{-5}	1.71×10^{-1}	8.56×10^{-2}	5.71×10^{-2}
Carbon tetrachloride	3.08×10^{-5}	5.87×10^{-2}	5.87×10^{-2}	3.92×10^{-2}
Chlorobenzene	3.42×10^{-5}	7.83×10^{-2}	7.83×10^{-2}	5.23×10^{-2}
Diethyl ether	3.49×10^{-5}	8.39×10^{-2}	8.39×10^{-2}	5.60×10^{-2}
Ethyl acetate	3.68×10^{-5}	1.70×10^{-1}	8.48×10^{-2}	8.45×10^{-2}
Methyl formate	3.21×10^{-5}	1.90×10^{-1}	9.49×10^{-2}	6.33×10^{-2}

Table 9 : Reduced zero-point energies of the investigated fluids; using only Sugden's data.

Geometric mean parameteres

Substance	ϵ_{12g}	ϵ_{13g}	ϵ_{23g}	ϵ_{123g}
Benzene	2.30×10^{-8}	3.28×10^{-3}	1.20×10^{-6}	4.50×10^{-6}
Carbon tetrachloride	3.24×10^{-8}	2.69×10^{-3}	1.41×10^{-6}	4.97×10^{-6}
Chlorobenzene	2.98×10^{-8}	3.27×10^{-3}	1.43×10^{-6}	5.19×10^{-6}
Diethyl ether	2.90×10^{-8}	3.42×10^{-3}	1.42×10^{-6}	5.20×10^{-6}
Ethyl acetate	3.20×10^{-8}	3.53×10^{-3}	1.53×10^{-6}	5.58×10^{-6}
Methyl formate	2.17×10^{-8}	3.49×10^{-3}	1.18×10^{-6}	4.48×10^{-6}

Table 10: Calculated values of surface tension for several fluids using Eq.26.

Substance	In contact with	T °C	σ dyn/cm	
			Obs.*	Cal.
Acetaldehyde	vapor	20	21.20	18.42
Aceton	air or vapor	20	23.70	22.25
Benzonitrile	air	20	39.20	38.10
Bromobenzene	air	20	36.5	39.89
Carbon dioxide	vapor	20	1.16	1.18
Chlorine	vapor	20	18.4	18.7
Chloroform	air	20	27.14	29.99
Cyclohexane	air	20	25.5	24.7
Ethylbenzene	vapor	20	29.20	29.10
Ethyl formate	air or vapor	20	23.6	23.0
Helium	vapor	-269	0.12	0.63
Hydrogen	vapor	-255	2.31	2.91
Hydrogen cyanide	vapor	17	18.2	16.42
Methyl acetate	air or vapor	20	24.6	22.88
Methyl chloride	air	20	16.2	15.54
Methyl propionate	air or vapor	20	24.9	22.51
Naphthalene	air or vapor	127	28.8	28.8
Neon	vapor	-248	5.50	7.92
Nitrogen	vapor	2183	6.6	7.06

* Taken from Ref.(10) .

Table 10 : (continued)

Substance	In contact with	T °C	σ dyne/cm	
			Obs.	Cal.
n-Octane	vapor	20	21.80	21.23
Oxygene	vapor	-183	13.2	15.17
Phenetole	vapor	20	32.74	31.02
Tolune	vapor	20	28.55	28.6

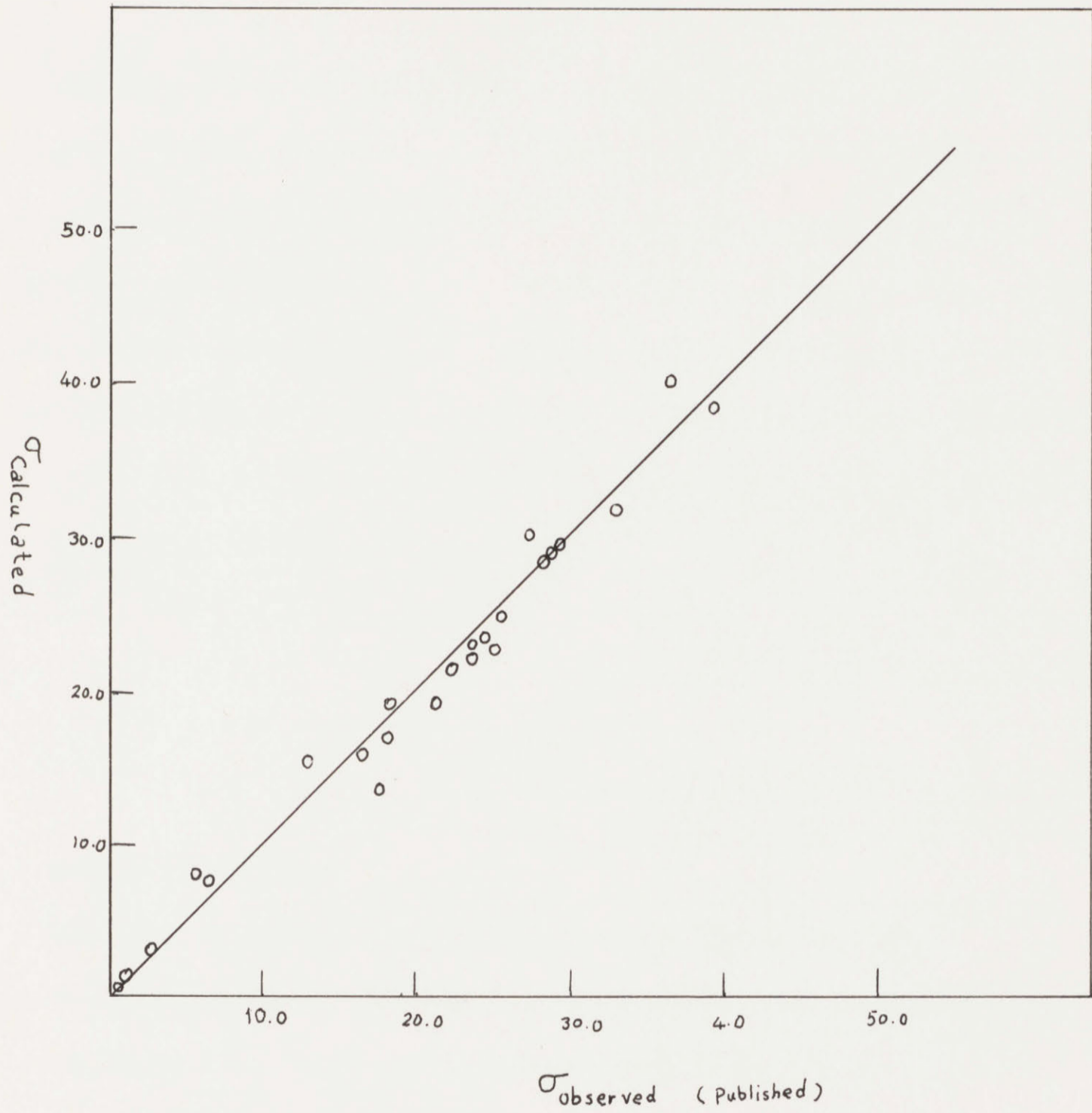


Fig.1 : Comparison between calculated values of surface tension and published values of surface tension.

Nomenclature

E = total surface energy
 E_0 = zero-point energy
 g_0 = acceleration of gravity
 M = molecular weight
 P_c = critical pressure
 T = temperature
 T_c = critical temperature
 V_c = critical volume

Greek

σ = surface tension
 σ_0 = surface tension at absolute zero temperature
 ϵ_{ijk} = reduced surface energy at zero absolute temperature
 μ = exponent in surface tension equation
 ρ_c = critical density
 ρ_l = density of the liquid phase
 ρ_v = density of the vapor phase

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Appendix A

On numerical differentiation*:

Numerical differentiation was employed to calculate the total surface energies from data on surface tension and temperature using the equation

$$E_{\sigma} = \sigma - T \frac{d\sigma}{dT}. \quad (30)$$

The general technique is outlined below:

If $F(X)$ is a function passing through $n+1$ equally spaced points X_k , $X_{k-1} = X_k - h$, $X_{k-2} = X_k - 2h, \dots, X_{k-n} = X_k - nh$, using the abbreviation $F_r = F(X_r)$, for central difference notation, we have:

$$F_r - F_{r-1} = \delta F_{r-1/2}$$

$$\delta F_{r+1/2} - \delta F_{r-1/2} = \delta^2 F_r$$

$$\delta^2 F_r - \delta^2 F_{r-1} = \delta^3 F_{r-1/2}$$

so that the subscripts of a difference is the mean of the subscripts of its parents.

If

$$X = X_0 + S \cdot h$$

Then by "Interpolation of Gauss" :

* See Ref. (11).

$$F(X_0 + S.h) \cong F_0 + S F_{1/2} = [S(S-1)/2!] \delta^2 F_0 + [S(S^2-1)/3!] \delta^3 F_{1/2} + [S(S^2-1)(S-2)/4!] \delta^4 F_0 + \dots$$

since

$$F'(X) = dF(X)/dX = h^{-1} dF/dS$$

then

$$F'(X_0 + S.h) = h^{-1} (\delta F_{1/2} + [2(S-1)/2!] \delta^2 F_0 + [3(S^2-1)/3!] \delta^3 F_{1/2} + \dots)$$

This equation was applied only to the data points which were equally spaced.

Corresponding to the problem of zero-point energy the following equalities hold:

$$X = T$$

$$F = \sigma$$

$$h = T_n - T_{n-1} = \Delta T$$

$$F'(X_0 + S.h) = d\sigma/dT$$

$$\delta F_{1/2} = F_1 - F_0$$

$$\delta^2 F_0 = \delta F_{1/2} - \delta F_{-1/2}$$

$$\delta^3 F_{1/2} = \delta^2 F_1 - \delta^2 F_0$$

$$S = 0.0 \text{ or } 1.$$

"S" was assigned the value 0 whenever the number of data points was sufficient for calculations. Otherwise S = 1.

Calculated values of dσ/dT was multiplied by (-T), and was added to σ at the same temperature to arrive at E_σ.

Appendix B

Calculation of zero-point energy for Ethyl acetate using Sugden's data :

σ d/cm	T °C	ΔT	$\delta\sigma$	$\delta^2\sigma$	$\delta^3\sigma$	$-\frac{d\sigma}{dT}$	$-T\frac{d\sigma}{dT}$	$E_\sigma = \sigma - T\frac{d\sigma}{dT}$ erg/cm ²
15.74	90	30	-3.66					
12.08	120	30	-3.23	0.43	-0.35	0.1129	44.38	56.46
8.85	150	30	-3.15	0.08	+0.31	0.1081	45.72	54.57
5.70	180	30	-2.76	0.39	-0.07	0.0981	44.46	50.16
2.94	210	30	-2.44	0.32		0.0863	41.69	44.64
0.50	240							

Appendix B (Continued)

Assuming $\mu = 1.23$,

T °K	σ d/cm	E_{σ}	A	B	AxB	E_o erg/cm ²
393.15	12.08	56.46	1.173	0.726	0.852	66.27
423.15	8.85	54.57	1.189	0.684	0.811	67.29
543.15	5.70	50.16	1.199	0.630	0.755	66.44
483.15	2.94	44.64	1.212	0.554	0.672	66.43

where A = (1 + 0.23 T/Tc), and B = (1 - T/Tc)^{0.23}

The following systems of equations were formed:

$$E_o = a\sigma + b$$

$$66.27 = a(12.08) + b$$

$$67.29 = a(8.85) + b$$

$$66.44 = a(5.70) + b$$

$$66.43 = a(2.94) + b$$

$$266.4 = a(29.57) + 4b$$

Solving for a and b :

$$a = 1.608 \times 10^{-2}$$

$$b = 66.48$$

$$E_o \times \sigma = a\sigma^2 + \sigma \times b$$

$$800.5 = a(145.9) + (12.08)b$$

$$595.5 = a(73.32) + (8.85)b$$

$$378.7 = a(32.49) + (5.70)b$$

$$195.3 = a(8.64) + (2.94)b$$

$$1970. = a(265.3) + (29.75)b$$

The value of the exponent was changed by ± 0.01 until a was at the vicinity of zero.