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ORGANIC SOLUTES IN PARAFFIN SOLVENTS

INFLUENCE OF THE SIZE OF THE SOLVENT MOLECULE ON SOLUTION DATA[a]

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SUMMARY

Solution properties at ideal dilution were measured for 124 solute probes by gas chromatography on five pure paraffins of well defined molecular weight at temperatures of 110–190°C. Standard chemical potential differences, related to the molal Henry coefficient, were calculated from retention data. Their temperature dependence allowed the calculation of partial molar solution enthalpy, entropy and heat capacity differences between the ideal gas phase and the ideal dilute solution. It was found that the standard chemical potential difference depended linearly on the variable $\zeta = 1000/M_L$, where M_L is the molecular weight of the paraffin stationary phase. The linear dependence was best explained by assuming that it is due to the linear dependence of the partial molar solution entropy of the solute on the variable ζ. Consequently, on a molal basis, a solute forms equithermal solutions in any of the liquid paraffins. Comparison with literature data suggested that these results have general validity. Approximate relationships are given to calculate the coefficient of variation of the retention index with temperature and with the variable ζ from thermodynamic data.

INTRODUCTION

Solute properties at ideal dilution in a family of homologous high-molecular-weight solvents are best investigated in terms of a standard chemical potential difference related to the molal Henry coefficient of the solute in the solvent[1–3]:

$$\Delta\mu_j^{(g)} = RT \ln [g_j/(\text{atm kg mol}^{-1})] \qquad \text{cal mol}^{-1} \quad (1)$$

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where R (= 1.9872 cal mol^{-1} K^{-1}) is the ideal gas constant, T (K) is the absolute temperature and g_j the molal Henry coefficient of the solute, j, defined by

$$g_j = P_j/\hat{m}_j \qquad \text{atm kg mol}^{-1};\ \hat{m}_j \text{ and } P_j \rightarrow 0 \tag{2}$$

The symbol P_j (atm) is for the partial pressure of the solute in equilibrium with the ideal dilute solution where the solute concentration is given in molality, $\hat{m}_j$ (mol kg^{-1}). This definition will be used throughout this paper and therefore the superscript (g) will be dropped for simplicity.

The temperature dependence of the standard chemical potential difference is described, at higher temperatures in a wide temperature range around a reference temperature $T^{\dagger}$ (at least ±100 K), with an adequate precision by

$$\Delta\mu_j = \Delta H_j - T\Delta S_j + \Delta C_{P,j}\left[T - T^{\dagger} - T\ln\left(\frac{T}{T^{\dagger}}\right)\right] \tag{3}$$

where ΔH_j and ΔS_j are the partial molar standard enthalpy and entropy differences of the solute between the ideal dilute solution and the ideal gas state at the reference temperature $T^{\dagger}$ (ref. 4). It was assumed that the difference in the partial molar heats of the solute between the two states, $\Delta C_{P,j}$, is constant in the temperature range in question (Kirchhoff's approximation), which results in the third term in eqn. 3.

With the specific definition of the standard chemical potential difference, the thermodynamic functions are differences between the reference states: unit molal concentration of the solute in 1 kg of solvent and the ideal gaseous state at unit pressure (1 atm). In an ideal gas there are no forces between the molecules. Therefore, the molar enthalpy can be considered as a measure of the interaction forces between solute and solvent molecules where solutes are surrounded only by solvent molecules contained in unit mass of solvent.

In a model family of solvents the solvent molecule is composed of identical building blocks (segments, monomers)[5–14]. Members of the solvent family will have molecules composed of different numbers of building blocks linked by chemical bonds. One kilogram of solvent will, therefore, contain the same number of building blocks, independent of the temperature and of the molecular weight of the solvent molecule. Thus, the solute is always attracted by the same number of building blocks and might have the same dissolution enthalpy in any member of the solvent family. The solute will form equithermal solutions with the members of the solvent family.

Less obvious is the effect of the choice of these standard states on the molar entropy of dissolution for which a standard state of constant volume would be preferable. The volume of 1 kg of solvent will obviously depend on the temperature and on the molecular weight of the solvent molecule. The "free volume" between the solvent molecules will be higher if the density is lower, introduced either by temperature or by a lower molecular weight. Therefore, the change in density will appear as an entropic effect.

A non-thermodynamic choice had to be made for the variable characterizing a specific member of the solvent family. It has been proposed[1,2] that a variable be introduced, proportional to the number of molecules in 1 kg of solvent. The variable ζ defined by

$$\zeta = 1000/M_L \qquad \text{mol kg}^{-1} \tag{4}$$

(M_L is the molecular weight of the solvent molecule) is proportional to the number of molecules in unit mass, if the (generally higher) weight of end-groups can be neglected [if necessary, a corrected variable $\zeta' = 1000/(M_L + k)$ may be used[1]. The choice of this variable is also justified by the results of the application of the lattice theory to the mixture of molecules of unequal size[4–14]. In the original theory of Flory[6] and Huggins[7–9], ζ appears as the natural variable for a mixture of molecules of unequal size at ideal dilution.

It is now proposed to describe the dependence of the chemical potential on the molecular weight of the solvent following the equation

$$\Delta\mu_j = {}^{\infty}\Delta\mu_j + \boldsymbol{R}_j\zeta \tag{5}$$

where ${}^{\infty}\Delta\mu_j$ is the standard chemical potential difference of the solute in a hypothetical member of the solvent family having infinite molecular weight ($\zeta = 0$) and $\boldsymbol{R}_j$ is a residual function. Formal comparison of eqn. 5 with eqn. 3 shows that this form of dependence may be the result of the variation of the partial molar enthalpy or that of the molar entropy (or of both) following the equations

$$\Delta H_j = {}^{\infty}\Delta H_j + h_j\zeta \tag{6}$$

$$\Delta S_j = {}^{\infty}\Delta S_j + s_j\zeta \tag{7}$$

where ${}^{\infty}\Delta H_j$ and ${}^{\infty}\Delta S_j$ are the partial molar enthalpy and entropy difference of the solute in the solvent of infinite molecular weight and the ideal gas state at $T^{\dagger}$, and h_j and s_j are the coefficients of variation of these functions with the variable ζ. Obviously, the partial molar heat difference, $\Delta C_{P,j}$, also ought to vary in a similar manner:

$$\Delta C_{P,j} = {}^{\infty}\Delta C_{P,j} + c_{P,j}\zeta \tag{8}$$

It will be assumed, and also proved experimentally, that the variation of $\Delta C_{P,j}$ with ζ is negligible, *i.e.*, $c_{P,j} = 0$. Actually, in eqn. 3 the term with $\Delta C_{P,j}$ represents a small correction, describing the slight curvature of the plot of $\Delta\mu_j$ as a function of temperature.

Comparing eqns. 3, 5, 6 and 7, the residual function in eqn. 5, $\boldsymbol{R}_j$, may have the following form:

$$\boldsymbol{R}_j = h_j - Ts_j \tag{9}$$

In fact, $\boldsymbol{R}_j\zeta$ is the difference in the standard chemical potential difference of the solute between the solution in a given solvent and that in the hypothetical solvent of infinite molecular weight ($\zeta = 0$). If the enthalpic coefficient $h_j = 0$, all solutions are equithermal, and the variation of the solution properties of the solute with the size of the solvent molecule is due only to entropic effects.

The objective of this work was the experimental study of the coefficients of eqn. 9 in the family of the simplest organic solvents, the paraffins. The same project has already been undertaken by using paraffins of series A, shown in Fig. 1, as stationary liquids[2,3]. However, the results were unsatisfactory. Because of the volatility of the

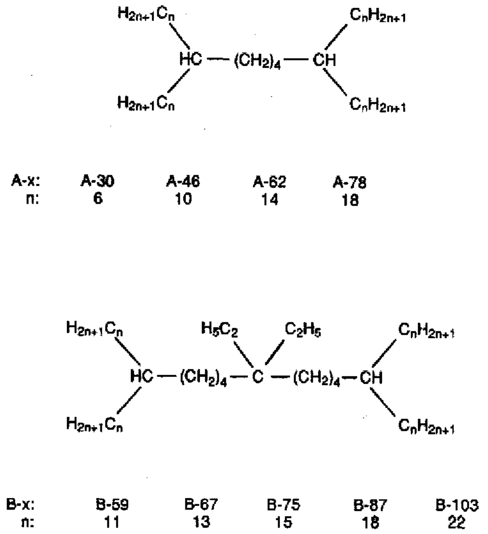

Fig. 1. Structure of paraffins, C_xH_{2x+2}, used in ref. 3 (series A) and in this work (series B) as stationary liquid.

paraffins A-30 and A-46, solution data at higher temperatures could not be determined and the experimental design was unbalanced for most solutes. The present project was designed on the basis of these experiences.

For the present project a series of five branched paraffins, B-x, of the general formula shown in Fig. 1, were synthesized to be used as stationary liquids[15]. n-Paraffins of the same molecular size could not be applied as stationary liquids because they had too high melting points. From the data listed in Table I, it is seen that the inverse molecular weight of the branched paraffins decreases by nearly equidistant steps in the series B-59 to B-103. The molecular weight of the smallest member, B-59, is such that it can be used up to about 200°C as a stationary phase without weight loss by evaporation and the molecular weight of the highest member, B-103, was chosen to have a melting point permitting it to be used from about 90°C as a stationary liquid[15]. Actually, this temperature is far enough from its melting point to exclude some nematic order in the B-103 liquid. The density of these paraffins has been determined up to 200°C[16] and it has been shown that it can be given for the whole family with a precision better than 0.1% by the equation[17]

$$\ln \rho = \ln {}^{\infty}\rho^{\dagger} + c_0^{\dagger}\,\zeta - {}^{\infty}\alpha^{\dagger}\Delta T + c_1\zeta\Delta T + c_2\zeta\Delta T^2 \qquad (10)$$

where ${}^{\infty}\rho^{\dagger}$ is the density of the hypothetical liquid paraffin of infinite molecular weight at the standard temperature $T^{\dagger}$, ${}^{\infty}\alpha^{\dagger}$ is the coefficient of thermal expansion of this same hydrocarbon and $c_0^{\dagger}$, c_1 and c_2 are constants. Column packings of high loading (10%, weight/total weight) were prepared with each paraffin in order to minimize the effect of adsorption of the solute at the solid support–liquid interface. It has been shown on the example of the B-87 hydrocarbon that adsorption at the liquid–gas interface is negligible[18].

TABLE I

PROPERTIES OF PARAFFIN STATIONARY LIQUIDS OF THE GENERAL FORMULA C_xH_{2x+2} OF THE SERIES B-*x*

In parentheses is given the number of carbon atoms in the side-chain (see Fig. 1). The symbol M is for molecular weight, ζ is as defined, $\rho^\dagger$ is for density, $v^\dagger$ is for molar volume, $\alpha^\dagger$ is the isobaric coefficient of thermal expansion at the standard temperature $T^\dagger = 130.0 + 273.15$ K and $A = 1/2\, d\alpha/dT$. Experimental data from ref. 16 are given in italics. The thermophysical data are smoothed values calculated according to eqn. 10 with the coefficients shown in the last line ($\rho^\dagger$ is the density at 130°C)[a].

L		*Elemental formula*	*m.p. (°C)*	*M (g mol⁻¹)*	$\zeta = 1000/M$ *(mol kg⁻¹)*	$\rho^\dagger$ *(g cm⁻³)*	$v^\dagger$ *(cm³ mol⁻¹)*	$\alpha^\dagger \cdot 10^4$ *(K⁻¹)*	$A \cdot 10^7$ *(K⁻²)*
B-x	*(n)*								
B-59	(11)	$C_{59}H_{120}$	5.5–7.0	829.61	1.20539	0.7695 *(0.7700)*	1078 *(1077)*	7.89 *(7.84)*	2.64 *(2.78)*
B-67	(13)	$C_{67}H_{136}$	13.5–14.5	941.83	1.06176	0.7720 *(0.7720)*	1220 *(1220)*	7.79 *(7.78)*	2.33 *(2.63)*
B-75	(15)	$C_{75}H_{152}$	22.5–23.5	1054.04	0.94873	0.7740 *(0.7745)*	1362 *(1361)*	7.70 *(7.76)*	2.08 *(2.22)*
B-87	(18)	$C_{87}H_{176}$	37.5–38.5	1222.37	0.81808	0.7763 *(0.7760)*	1575 *(1575)*	7.61 *(7.64)*	1.79 *(1.76)*
B-103	(22)	$C_{103}H_{208}$	47.5–48.5	1446.80	0.69118	0.7786 *(0.7775)*	1858 *(1861)*	7.51 *(7.51)*	1.51 *(0.61)*
B-∞	(∞)	$C_\infty H_\infty$	~140	∞	0	0.7910 (–)	∞ (–)	7.00 (–)	0.00 (–)

[a] $\ln {}^\infty\rho^\dagger = -0.2485$; ${}^\infty\alpha^\dagger = 7.00 \cdot 10^{-4}$; $c_0^\dagger = -0.02439$ (series A, -0.03021); $c_1 = -8.30 \cdot 10^{-5}$ (series A, $-8.95 \cdot 10^{-5}$); $c_2 = -2.19 \cdot 10^{-7}$ (series A, -1.50 10^{-7}).

With each packing two columns were prepared with a known amount of stationary liquid and specific retention volumes of seven *n*-alkanes, C_zH_{2z+2}, with $z = 5$–11 were determined at every 10 K in the temperature interval between 110 and 190°C. Molal Henry coefficients were calculated with the aid of

$$g_z = \mathcal{R}T/1000\ V_{g,z} \tag{11}$$

where $\mathcal{R}$ is the ideal gas constant ($\mathcal{R} = 82.0575$ cm^3 atm mol^{-1} K^{-1}) and $V_{g,z}$ [cm^3 g^{-1}] is the specific retention volume of the alkane with carbon number z. The set of $9 \times 5 \times 7 = 315$ chemical potentials, calculated with eqn. 1, were then analysed as a complete factorial design (see, *e.g.*, ref. 19) with the factors T = temperature (110–190°C; nine equidistant levels), L = stationary liquid ($\zeta = 0.9450$–1.2054 mol kg^{-1}; five nearly equidistant levels) and S = alkane solutes ($z = 5$–11; seven equidistant levels) as explained under Experimental. This analysis of variance permitted a representation of the experimental domain with the aid of orthogonal polynomials where only significant terms were considered. Standard chemical potential differences were now calculated from this expression for every alkane at every 10 K between 110 and 190°C. Using these points, the thermodynamic functions were then determined as the coefficients of eqn. 12 by a non-linear regression with $T^{\dagger} = 130.0 + 273.16$ K as the reference temperature.

$$\Delta\mu_j = {}^{\infty}\Delta H_j + \zeta h_j - T\,{}^{\infty}\Delta S_j - T\zeta s_j + \Delta C_{P,j}\left[T - T^{\dagger} - T\ln\left(\frac{T}{T^{\dagger}}\right)\right] \tag{12}$$

Parallel to these experiments, retention indices were determined for a series of chosen solutes in general at 110, 130, 150, 170 and 190°C. The results were evaluated in two ways. First, the coefficients of eqn. 13 were determined by the method of least squares. Also a variant was calculated where the coefficient $A_{T,\zeta}$ was put equal to zero.

$$I = {}^{\infty}I^{\dagger} + A_T\Delta T + A_\zeta\zeta + A_{T,\zeta}\zeta\Delta T \tag{13}$$

where ${}^{\infty}I^{\dagger}$ is the retention index of the solute on the stationary phase of infinite molecular weight at 130°C, A_T, A_ζ and $A_{T,\zeta}$ are regression coefficients and $\Delta T = T - T^{\dagger}$ with $T^{\dagger} = 130.0 + 273.15$ K. In a second evaluation, retention indices were transformed one by one to standard chemical potential differences by linear interpolation between the chemical potentials of suitable *n*-alkanes based on the relationship[20]

$$I_j = 100 \cdot \frac{\Delta\mu_j - \Delta\mu_z}{\Delta\mu_{z+1} - \Delta\mu_z} + 100z \tag{14}$$

where $\Delta\mu_z \leqslant \Delta\mu_j \leqslant \Delta\mu_{z+1}$. Using the resulting points, the functions ${}^{\infty}\Delta H_j$, ${}^{\infty}\Delta S_j$, $\Delta C_{P,j}$, h_j and s_j were determined as coefficients of eqn. 12 by non-linear regression.

BASIC RELATIONSHIPS

In gas chromatography, the net retention volume, $V_{N,j}$, of the solute j is related to the distribution coefficient at infinite dilution by eqn. 15 if the following conditions hold: solute vapour in the eluent can be considered as a mixture of ideal gases; the solute is not adsorbed at the support–stationary liquid and stationary liquid–gas interfaces; and the solute is at infinite dilution in both phases.

$$V_{N,j} = W_L\, K_{D,j} \tag{15}$$

where W_L is the volume of the stationary phase in the column and the distribution coefficient is defined by

$$K_{D,j} = [j]_L/[j]_\mu = \mathcal{R}T\,[j]_L/1000P_j; \qquad [j]_\mu \rightarrow 0 \tag{16}$$

where $[j]$ represents the molar concentration of the solute, j, in the stationary liquid, L, and mobile phase, μ, respectively. The right-hand side of eqn. 16 is only valid under the above-mentioned conditions. The Bunsen coefficient, the Henry coefficient and the molal Henry coefficient are defined in eqns. 17, 18 and 2.[4]

$$b_j = [j]_L/P_j; \qquad P_j \rightarrow 0 \tag{17}$$

$$h_j^* = P_j/x_j; \qquad P_j \rightarrow 0 \tag{18}$$

where P_j is the partial pressure of the solute in the mobile phase and x_j is the molar fraction of the solute in the stationary phase. The specific retention volume is defined by

$$V_{g,j} = V_{N,j}/w_L \tag{19}$$

where w_L is the mass of the stationary liquid in the column. Using the definitions of the coefficients K_D, b, h^* and g (eqns. 16, 17, 18 and 2), the definition of the specific retention volume (eqn. 19), the relationship of eqn. 11 and the equation of state of the ideal gas, the relationships summarized in eqn. 20 are derived.

$$V_{g,j} = \tilde{v}_L\, K_{D,j} = \frac{\tilde{v}_L\, b_j\, \mathcal{R}T}{1000} = \frac{\mathcal{R}T\zeta}{1000h_j^*} = \frac{\mathcal{R}T}{1000g_j} \tag{20}$$

where $\tilde{v}_L$ (cm^3 g^{-1}) is the specific volume of the stationary liquid $[\tilde{v}_L = \tilde{v}_L(T,\zeta)]$ and the other symbols are as before.

The retention index is defined by

$$I_j = 100\,\frac{\log V_{g,j} - \log V_{g,z}}{\log V_{g,z+1} - \log V_{g,z}} + 100z \tag{21}$$

$$V_{g,z} \leqslant V_{g,j} \leqslant V_{g,z+1}$$

Eqn. 14 is derived by substituting either the relationship between $V_{g,i}$ and K_D, b, h^* or g summarized in eqn. 20 for $V_{g,j}$ in eqn. 21 and multiplying the right-hand side of this equation by RT/RT^{20}. It is then observed that eqn. 12 is valid for the standard chemical potential difference related to the molal Henry coefficient, $\Delta\mu_j$, but also for those defined in eqns. 22, 23 and 24.

$$\Delta\mu_j^{(D)} = -RT \ln K_{D,j} \tag{22}$$

$$\Delta\mu_j^{(b)} = -RT \ln [b_j/(\text{mol } 1^{-1} \text{ atm}^{-1})] \tag{23}$$

$$\Delta\mu_j^{(h^*)} = RT \ln [h_j^*/(\text{atm})] \tag{24}$$

EXPERIMENTAL

Materials

Solutes were research-grade compounds from Fluka (Buchs, Switzerland). The structure of the paraffins B-59, B-67, B-75, B-87 and B-103 used as stationary liquids is shown in Fig. 1. Some of the properties of these compounds, synthesized in our laboratory are listed in Table I[15,16]. Two batches of Volaspher A2 from Merck (Darmstadt, F.R.G.) were used as supports: batch Nos. 1120015 and 2328148. The commercial material was sieved and the fraction with particle diameter d_p = 150–180 μm was used. For the preparation of column packings, an exact amount of support (*ca.* 25 g weighed with a precision of ±0.01 g) was wetted with a 3% solution of one of the paraffins (*ca.* 3.00 g weighed with a precision of ±0.001 g) in 100 ml of cyclohexane. Under a gentle stream of argon (<1 ppm of oxygen), the solvent was evaporated at 60–70°C in a slowly rotating evaporator, then the temperature was raised to 200°C for 1.0 h. Column packings were stored in an argon atmosphere. Columns (coiled Pyrex tubes of I.D. 0.40 cm and length 330 cm) were packed with the column material under vibration. The weight of the packing in the column (calculated as the difference of the weight of the packed and empty column) is given in Table II. Immediately after packing the columns were filled with argon, and those in use with helium.

Apparatus

The apparatus used for the determination of retention data is described in detail in ref. 18. In summary, a slightly modified Packard-Becker (Delft, The Netherlands) Model 419 chromatograph was used, equipped with two thermal conductivity detectors. The temperature of the two columns in the oven thermostat was measured with a Pt sensor (100 Ω; DIN 43710) and a measuring device from Systemteknik (Lidingoe, Sweden; Model S 1220). The Pt sensor was calibrated by the "Eidg. Amt für Mass und Gewichte" (Bern, Switzerland) between 0 and 400°C with a precision of ±0.1 K. The temperature gradient in the oven was measured with chromel–alumel thermocouples at eight points. The mean column temperature was calculated by considering the temperature gradient as described in ref. 18.

TABLE II

CHARACTERISTICS OF THE CHROMATOGRAPHIC COLUMNS

w_L is the mass of the stationary liquid in the column, P_L is the percentage of L of the packing ($100w_L$/total mass). Support: Volaspher, batch No. 1120015. Also listed are correction factors, f_L, for the weight of the stationary liquid calculated on the basis of the analysis of variance (see eqn. 33 and text) of the retention data of *n*-alkanes.

Stationary liquid, B-x	*Column*	w_L *(g)*	P_L *(%)*	f_L
B-59	A	1.951	9.99	0.9999
	B	1.859	10.04	
B-67	A	1.896	9.99	0.9965
	B[a]	1.964	10.00	
B-75	A	2.105	9.97	1.0024
	B	2.061	10.03	
B-87	A	1.866	10.04	1.0057
	B	1.919	10.06	
B-103	A[a]	1.956	9.90	0.9955
	B[a,b]	1.571	10.06	

[a] Volaspher batch No. 2328148.

[b] Column length 230 cm (instead of 330 cm).

Retention volume

The retention time, $t_{R,j}$ (min), of a solute, j, was determined at the peak maximum with an integrator from Hewlett-Packard (Model 3390 A) with a reproducibility of ± 0.001 min. The retention time of neon, $t_{R,Ne}$ was used as the hold-up time for the calculation of the net retention time in the equation

$$t_{N,j} = t_{R,j} - t_{R,Ne} \tag{25}$$

The flow-rate of the carrier was measured at the column outlet at the temperature T_f (K) of the soap-film flow meter. The carrier was saturated with water vapour prior to the measurement. The reduced flow-rate, $\dot{V}_f^{(\mathrm{NTP})}$, was calculated using

$$\dot{V}_f^{(\mathrm{NTP})} = \dot{V}_f[(P_{\mathrm{atm}} - P_{\mathrm{H_2O}})/760]\,(273.15/T_f) \tag{26}$$

where $\dot{V}_f$ is the flow-rate of the saturated carrier at atmospheric pressure, P_{atm} (Torr), and $P_{\mathrm{H_2O}}$ (Torr) is the vapour pressure of water at the temperature T_f (K). The pressure drop on the column was measured with a precision manometer from Dresser Industries (Stratford, CT, U.S.A.; Ashcroft Digigauge). Inlet and outlet pressures of the column, P_{in} and P_{out}, were corrected for the flow resistance of the injector and the detector, respectively. The flow-rate in the column at the mean column temperature, T_c, and the mean column pressure, P_c, was calculated from

$$\dot{V}_c = \dot{V}_f^{(\mathrm{NTP})}\,(T_c/273.15)\,(760/P_{\mathrm{out}})\tfrac{2}{3}J \tag{27}$$

where

$$\tfrac{2}{3}J = (3/2)[(P_{\text{in}}/P_{\text{out}})^2 - 1]/[(P_{\text{in}}/P_{\text{out}})^3 - 1] \tag{28}$$

is the correction factor of James and Martin[21] for a homogeneous column bed and an ideal gas carrier. The specific retention volume is then given by

$$V_{g,j} = V_{N,j}/w_L = \dot{V}_c t_{N,j}/w_L \tag{29}$$

where w_L (g) is the mass of stationary liquid, L, in the column.

Retention volumes of the *n*-alkane solutes (C_zH_{2z+2}, $z = 5$–11) were determined on two columns of each of the five stationary phases at nominal temperatures T_c ranging from 110 to 190°C at every 10 K interval in the following way. The specific retention volume was determined at a temperature T_{exp} near the nominal temperature, T_c, where $\delta T = T_c - T_{\text{exp}}$ never exceeded ± 0.5 K. At least four independent determinations were made at temperatures near 110, 130, 150, 170 and 190°C and at least two at 120, 140, 160 and 180°C. Average specific retention volumes were calculated on each of the columns which were in turn averaged to give the experimental specific retention volumes given in the equation

$$V_{g,\text{exp},z} = \frac{\bar{V}^{(\text{A})}_{g,z} + \bar{V}^{(\text{B})}_{g,z}}{2} \tag{30}$$

at $T_{\text{exp}} = [\bar{T}(\text{A}) + \bar{T}(\text{B})]/2$. Assuming a linear dependence of V_g on T in the small temperature domain, δT, the specific retention volume measured at T_{exp} was then corrected for the slight temperature deviation δT with the aid of the equation

$$V_{g,z}(T_c) = V_{g,z}(T_{\text{exp}}) \exp\left[\frac{\delta T}{T}\left(\frac{\Delta H_z}{RT} + 1\right)\right] \tag{31}$$

where $T \approx T_{\text{exp}}$ and ΔH_z is the molar enthalpy difference of the *n*-alkane z between the gas and the liquid phases at the temperature $T^{\dagger} = 130 + 273.15$ K. It was assumed that ΔH_z is nearly independent of the molecular weight of the paraffin stationary phase, and therefore values for these enthalpy differences were taken from ref. 18 (ΔH_z of the alkanes in the stationary liquid B-87). This approximation is justified by the results of the present study. As an example, this correction represents, for $\delta T = \pm 0.5$ K, a factor of about 1.00 ± 0.01 for the specific retention volume of pentane and 1.00 ± 0.02 for that of dodecane at the lowest nominal temperature of 110°C.

The results of these experiments gave a table of specific retention volumes of the seven *n*-alkanes with $z = 5$–11 on the five paraffin stationary phases B-59, B-67, B-75, B-87 and B-103 at every 10 K interval between 110 and 190°C. Retention volumes of dodecane and tridecane were also determined but only at higher temperatures: $z = 12$ at $T = 150$–190°C and $z = 13$ at $T = 160$–190°C.

Standard chemical potentials

Molal Henry coefficients were calculated from the corrected specific retention volumes with eqn. 11 and the standard chemical potential difference with eqn. 1 to give a set of 315 standard chemical potential differences at the nominal temperatures. This set was used for the following analysis of variance.

Analysis of variance and correction of the measured chemical potential for weighing errors

Analysis of variance of the standard chemical potential differences of the *n*-alkane solutes shown in Table III refers to the description of the experimental domain by the equation

$$\begin{aligned} \Delta\mu = {} & b^{(0)} + b_T^{(1)}P_T^{(1)} + b_T^{(2)}P_T^{(2)} + b_L^{(1)}P_L^{(1)} + b_S^{(1)}P_S^{(1)} + \\ & + b_S^{(2)}P_S^{(2)} + b_S^{(3)}P_S^{(3)} + b_S^{(4)}P_S^{(4)} + b_{T,L}^{(1,1)}P_T^{(1)}P_L^{(1)} + b_{T,S}^{(1,1)}P_T^{(1)}P_S^{(1)} + \\ & + b_{T,S}^{(1,2)}P_T^{(1)}P_S^{(2)} + b_{T,S}^{(2,1)}P_T^{(2)}P_S^{(1)} + b_{T,S}^{(1,3)}P_T^{(1)}P_S^{(3)} + b_{L,S}^{(1,1)}P_L^{(1)}P_S^{(1)} \end{aligned} \qquad (32)$$

where $P_X^{(i)}$ is an orthogonal polynomial of the degree i related to the effect $X = L, T$ and S and $b_X^{(i)}$ is the corresponding regression coefficient[22]. The polynomials designated by the subscript L refer to the five levels of the nearly equidistant variable $\zeta = 1000/M_L$, where M_L is the molecular weight of the stationary liquid. They were calculated following ref. 19 to give the values listed in Table IV. The polynomials designated by T, defined at nine equidistant temperatures $T - 273.15 = 110.0$–190.0°C (steps of 10 K) and those designated by S, defined at the seven equidistant values of $z = 5$–11 for the *n*-alkane solutes C_zH_{2z+2}, were taken from ref. 22. Only significant terms are listed in eqn. 32.

First, an analysis of variance was performed on this set of 315 standard chemical potential differences. The result of this analysis is seen in Table III if the corresponding figures are substituted by those indicated in footnote *a*. It is observed that several variances of the subspace *TL* are highly significant against the estimate of the experimental error, $V'(TLS)$, such as $V'[T^{(1)}L^{(1)}]$ and the residual variance of the effect *TL*, $V'(\text{res. } TL)$. Tested against this variance also systematic quadratic, cubic and quartic variations of $\Delta\mu$ on the inverse of the molecular weight of L were highly significant; a fact very improbable for thermodynamic reasons (except perhaps a quadratic term). On the other hand, variances such as $V'[T^{(1)}L^{(2)}]$ and $[T^{(2)}L^{(1)}]$ were non-significant. These results suggest that the error in the *TL* subspace is different from the final estimate of the residual variance by equating the latter to $V'(TLS)$. It is logical to consider that the error introduced by adjusting a new temperature or by changing the column is more important than that which is observed on the same column during a working day. It was therefore concluded that $V'(\text{res. } TL)$ is due to a stochastic error introduced by changing T and L and that variances of this subspace are to be tested against this variance. Testing against $V'(\text{res. } TL)$, the linear dependance of $\Delta\mu$ on L is highly significant. Also, the residue $V'(\text{res. } L)$ (including linear to quartic terms) remained significant. We believe that this highly significant error in the dependence on ζ is due to stochastic weighing errors in the determination of the mass of the stationary liquid in the column. The true mass of the stationary liquid in the column is given by

$$w_L = f_L w_{L,\mathrm{exp}} \qquad (33)$$

TABLE III

ANALYSIS OF VARIANCE OF THE SET OF 315 STANDARD CHEMICAL POTENTIALS OF THE *n*-ALKANE SOLUTES

Data were corrected for weighing errors of the stationary liquid in the column (see eqn. 33 and Table II). The source of variance is related to the orthogonal terms in eqn. 32. $X^{(i)}$ is the systematic polynomial variation of $\Delta\mu$ on the effects T (temperature), S (carbon number of the solute) and L (the inverse of the molecular weight of the stationary liquid). The superscript in parentheses refers to the degree of the orthogonal polynomial: (1) linear; (2) quadratic; (3) cubic; (4) quartic. SQ is the sum of squares, Φ is the number of degrees of freedom and V' is the combined variance to be analysed by Fisher's F. The coefficients $b_x^{(i)}$ in eqn. 32 are also listed. The abbreviation res. is for "residual variance" and id. means that V' is identical to the corresponding SQ.

Source		*SQ*	Φ	V'	*F*	*Significance (%)*	$b_x^{(i)}$
X	*(i)*						
$\Delta\bar{\mu}$	(0)		1				−245.9
T	(1)	75 746 554.4	1	id.	$4.65 \cdot 10^5$	0.01	+189.92
	(2)	19 218.7	1	id.	$1.18 \cdot 10^2$	0.01	−1.335
	(res. T)^{*a}	1656.9	6	276.2		—	
L	(1)^{a}	324 262.0	1	id.	$1.99 \cdot 10^3$	0.01	−178.3
	(res. L)^{b}	0.0	3	0.0		—	
TL	(1,1)	1457.3	1	id.	8.96	1	−4.63
	(res. TL)^{*a,b}	4358.9	31	140.6			
1st res.	$(=\Sigma X^*)^{b}$	6015.8	37	162.6			
S	(1)	304 524 896.4	1	id.	$1.91 \cdot 10^7$	0.01	−491.6
	(2)	50 510.8	1	id.	$3.17 \cdot 10^3$	0.01	+0.3661
	(3)	2381.5	1	id.	$1.50 \cdot 10^2$	0.01	−0.495
	(4)	78.0	1	id.	4.90	5	+0.062
	(res. S)	10.8	2	5.4		—	
TS	(1,1)	1050 479.1	1	id.	$6.60 \cdot 10^4$	0.01	+11.18
	(1,2)	715.1	1	id.	$4.49 \cdot 10^1$	0.01	+0.17
	(2,1)	1922.0	1	id.	$1.21 \cdot 10^2$	0.01	−0.211
	(1,3)	58.1	1	id.	3.65	10	−0.030
	(res. TS)**	1193.2	44	27.1			
LS	(1.1)	2242.7	1	id.	$1.41 \cdot 10^2$	0.01	−7.4
	(res. LS)^{**c}	203.9	23	8.9		—	
TLS^{**c}		2747.5	192	14.3		—	
2nd res.	$(=\Sigma X^{**})$	4155.4	261	15.9			

[a] Important to note: after correction for weight of L the following terms are non-significant against 1st res: $SQ[\mathrm{T}^{(3)}] = 153.2$; $SQ[T^{(4)}] = 327.9$; $SQ[T^{(1)}L^{(2)}] = 15.4$; $SQ[T^{(2)}L^{(1)}] = 4.9$.

[b] Before correction for weight of L: SQ (res. L) = 3305.9 ($\Phi = 3$), significance 0.1% against V' (res. TL) = 145.3 (Φ = 31); SQ (res. TL) = 4504.4 (Φ = 31); SQ (1st res.) = 6161.3 (Φ = 37).

[c] Important to note: after correction for weight of L, the following terms are non-significant against 2nd res.: $SQ\ [L^{(1)}S^{(2)}] = 1.7$; $SQ\ [L^{(2)}S^{(1)}] = 1.0$; $SQ[T^{(1)}L^{(1)}S^{(1)}] = 1.6$.

where f_L is a correction factor. In order to estimate this factor, the dependence of the average of the chemical potential on the variable ζ was considered to be linear. In Fig. 2, the linear dependence is compared with the experimental points. If deviations from linearity are due only to weighing errors, then eqn. 34 holds.

$$\Delta\mu_j = RT \ln\left(\frac{\mathcal{R}T}{V_{g,j}\, f_L}\right) = \Delta\mu'_j - RT \ln f_L \tag{34}$$

TABLE IV

VALUES OF THE LINEAR AND QUADRATIC ORTHOGONAL POLYNOMIALS $P_L^{(1)}$ AND $P_L^{(2)}$ IN THE VARIABLE $\zeta = 1000/M_L$ CHARACTERIZING THE FIVE STATIONARY PHASES B-59–B-103

B-X	ζ^a	$\Delta\zeta$	$P_L^{(1)}$	$P_L^{(2)}$
B-59	1.20539		+0.26036	+0.03403
		0.14362		
B-67	1.06176		+0.11673	−0.01938
		0.11303		
B-75	0.94873		+0.00370	−0.03240
		0.13065		
B-87	0.81808		−0.12695	−0.01561
		0.12690		
B-103	0.69118		−0.25385	+0.03337

^{a} $\bar{\zeta} = 0.94503$.

where the deviation from the linear regression is identified as $-RT \ln f_L$. The calculated correction factors are listed in Table II.

Experimental chemical potential values, $\Delta\mu'_i$, were corrected with the aid of the factors f_L to give a new set of 315 standard chemical potential differences. This set was considered as the basis of all further calculations. The analysis of variance of this set and the coefficients $b_X^{(i)}$ in eqn. 32 are listed in Table III.

Estimation of the experimental error

An orthogonal term $V'(X)$ in an analysis of variance is composed of the contributions given in the equation[19]

$$V'(X) = V(\text{exp. error}) + v_X V(X) \tag{35}$$

where v_X is the number of statistical units composing a figure in the table having served to estimate $V'(X)$, and $V(X)$ is the variance due to the source X. The zero hypothesis, $V(X) = 0$, can therefore be proved or disproved by testing $V'(X)$ against an estimate of

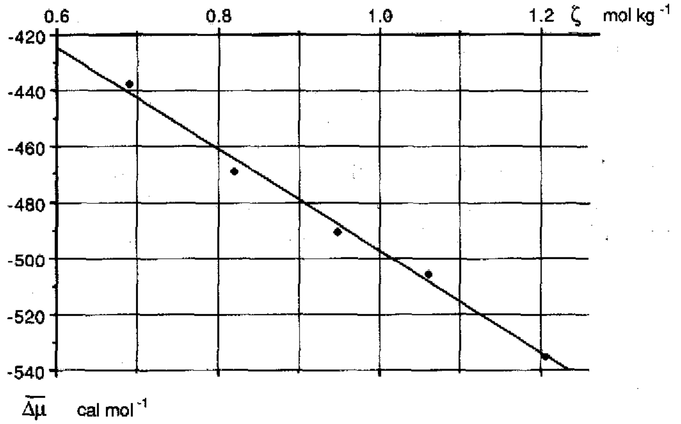

Fig. 2. Plot of the average standard chemical potential difference of seven *n*-alkanes at nine temperatures as a function of the inverse molecular weight of the stationary liquid.

the experimental error by using Fisher's test. In Table III, the variance of the experimental error was put equal to $V'(TLS)$ by assuming that $V(TLS) = 0$. Systematic highest order variations were shown to be non-significant by proving that terms such as $V'[T^{(1)}L^{(1)}S^{(1)}]$ are non-significant.

The standard deviation of a statistical unit is calculated from the "2nd res." in Table III as $\sigma_2 = \pm 4.0$ cal mol^{-1} ($\Phi = 261$) to give the confidence limit at the 95% confidence level of $\Delta_{95} = \pm 9.4$ cal mol^{-1}.

The residual variance V'(res. TL) is highly significant if tested against the "2nd res." It is believed that V'(res. TL) is due to stochastic errors, and not to an additional systematic dependence of $\Delta\mu$ on T and L. The non-significance of $V'[T^{(1)}L^{(2)}]$ and $V'[T^{(2)}L^{(1)}]$ supports this thesis. The corresponding variance can now be calculated with eqn. 35 after rearrangement:

$$V(\text{1st res.}) = [V'\ (\text{1st res.}) - V(\text{2nd res.})]/\nu_{TL} = (162.7 - 15.9)/7 = 20.9 \quad (36)$$

where $\nu_{TL} = 7$ (the number of n-alkanes). The result gives $\sigma_1 = \pm 4.6$ ($\Phi = 37$) and $\Delta_{95} = \pm 11.1$ cal mol^{-1}.

The result is interpreted as follows. Solutes are injected as mixtures during a working day where the temperature and column remain constant. During a working day, the chemical potential of an n-alkane is reproducible to $\Delta_{95} = \pm 9.4$ cal mol^{-1}. If new experimental conditions, T and L, are chosen, the error between the chemical potentials is $\Delta_{95} = \pm 11.1$ cal mol^{-1}. The variance of the total error is calculated as

$$V(\text{tot. error}) = 20.9 + 15.9 = 36.9 \quad (37)$$

to give Δ_{95} (tot. error) $= \pm 14.7$ cal mol^{-1}. We also conclude that the error of the chemical potentials calculated from retention indices should be around $\Delta_{95} = \pm 9.4$ cal mol^{-1}, these values having been calculated relative to the data of the n-alkanes.

Polynomial description of the standard chemical potential differences of the n-alkanes

With the aid of the polynomials $P_s^{(i)}$ and the corresponding coefficients $b_s^{(i)}$ (eqn. 32 and Table III), the coefficients $c_X^{(i)}$ in eqn. 38 were calculated to describe the dependence of $\Delta\mu$ of a given n-alkane in terms of $P_T^{(i)}$ and $P_L^{(i)}$.

$$\Delta\mu(n\text{-alkane}) = c_S^{(0)} + c_T^{(1)}P_T^{(1)} + c_T^{(2)}P_T^{(2)} + c_L^{(1)}P_L^{(1)} + c_{T,L}^{(1,1)}P_T^{(1)}\,P_L^{(1)} \quad (38)$$

where the symbols are as before. The values of the coefficient $c_X^{(i)}$ are given in Table V.

Orthogonal polynomials of higher degrees can be expressed as a function of the linear orthogonal polynomial following eqns. 39a and b (see ref. 22, p. 34).

$$P_X^{(1)} = \xi_X \quad (39a)$$

$$P_X^{(2)} = \xi_X^2 - \frac{N_X^2 - 1}{12} \quad (39b)$$

where ξ_X is a continuous variable equal to $P_X^{(1)}$ at the N_X discrete values where $P_X^{(1)}$ is

TABLE V

REGRESSION COEFFICIENTS FOR THE DESCRIPTION OF THE STANDARD CHEMICAL POTENTIAL DIFFERENCE OF AN *n*-ALKANE BY EQN. 38

z	$c_s^{(0)}$	$c_T^{(1)}$	$c_T^{(2)}$	$c_L^{(1)}$	$c_{T,L}^{(1,1)}$
5	1250.5	+157.39	−0.702	−156.0	−4.63
6	733.6	+167.38	−0.913	−163.4	−4.63
7	231.9	+178.05	−1.124	−170.9	−4.63
8	−259.2	+189.25	−1.335	−178.3	−4.63
9	−745.4	+200.78	−1.546	−185.7	−4.63
10	−1226.9	+212.47	−1.757	−193.1	−4.63
11	−1705.1	+224.13	−1.969	−200.5	−4.63

defined ($N_T = 9$, $N_S = 7$, $N_L = 5$). Substitution of eqns. 39a and b in eqn. 38 gives a polynomial expression in ξ_T and ξ_L where

$$\xi_T = (T - \bar{T})/10 \tag{40a}$$

$$\xi_L = \zeta - \bar{\zeta} \tag{40b}$$

In eqns. 40, $\bar{T} = 150.0 + 273.15$ K is the mean temperature and $\bar{\zeta} = 0.94503$ mol kg^{-1} is the average value of the variable ζ. Substitution of eqns. 40a and b in the resulting equation and introduction of the variable

$$\Delta T = 10\xi_T + 20 \tag{41}$$

gives eqn. 42 for the description of the chemical potential of an *n*-alkane as a function of the variable ζ around the standard temperature of $T^\dagger = 130.0 + 273.15$ K ($\Delta T = T - 403.15$ K).

$$\Delta\mu(n\text{-alkane}) = d^{(0)} + d_T^{(i)}\Delta T + d_T^{(2)}\Delta T^2 + d_L^{(1)}\zeta + d_{T,L}^{(1,1)}\zeta\Delta T \tag{42}$$

The value of the coefficients $d_X^{(i)}$ is given in Table VI.

Relationship between the coefficients $d_X^{(i)}$ and thermodynamic data

Substitution of $\Delta T = T - T^\dagger$ in eqn. 3 gives the dependence of $\Delta\mu$ of an *n*-alkane as a function of ΔH, ΔS and ΔC_p.

$$\Delta\mu(n\text{-alkane}) = \Delta H - T^\dagger\Delta S - \Delta S\Delta T + \Delta C_p[\Delta T - (T^\dagger + \Delta T)\ln(1 + \frac{\Delta T}{T^\dagger})] \tag{43}$$

Approximation of the logarithmic expression by a Taylor series and substitution of the result in eqn. 43 gives

$$\Delta\mu(n\text{-alkane}) = \Delta H - T^\dagger\Delta S - \Delta S\Delta T - \frac{\Delta C_p}{(1\times 2)\ T^\dagger}\cdot\Delta T^2 + $$

$$+ \frac{\Delta C_p}{(2\times 3)\ (T^\dagger)^2}\cdot\Delta T^3 - \frac{\Delta C_p}{(3\times 4)\ (T^\dagger)^3}\cdot\Delta T^4 + \ldots \tag{44}$$

TABLE VI

REGRESSION COEFFICIENTS $d_X^{(i)}$ FOR THE DESCRIPTION OF THE STANDARD CHEMICAL POTENTIAL DIFFERENCE OF AN *n*-ALKANE AS A POLYNOMIAL OF THE VARIABLES $\zeta = 1000/M_L$ (mol kg^{-1}) AND $\Delta T = T - 403.15$ K (EQN. 42)

z	$d^{(0)}$	$d_T^{(1)}$	$d_T^{(2)} \cdot 10^3$	$d_L^{(1)}$	$d_{T,L}^{(1,1)}$
5	1076.3	16.4573	−7.02	−146.74	−0.463
6	546.9	17.5407	−9.13	−154.14	−0.463
7	31.6	18.6921	−11.24	−161.64	−0.463
8	−475.1	19.8965	−13.35	−169.04	−0.463
9	−976.1	21.1339	−15.46	−176.44	−0.463
10	−1473.4	22.3873	−17.57	−183.84	−0.463
11	−1967.4	23.6381	−19.69	−191.24	−0.463

Comparison of eqns. 42 and 44 gives the desired relationships between the regression coefficients $d_X^{(i)}$ and the thermodynamic functions ΔH, ΔS and ΔC_p. In eqn. 45c, higher than quadratic terms in ΔT were not considered.

$$\Delta H - T^{\dagger}\Delta S = d^{(0)} + d_L^{(1)}\zeta \qquad (45a)$$

$$-\Delta S = d_T^{(1)} + d_{T,L}^{(1,1)}\zeta \qquad (45b)$$

$$-\Delta C_p/2T^{\dagger} = d_T^{(2)} \qquad (45c)$$

After rearrangement, eqns. 46a–c result:

$$^{\infty}\Delta H = d^{(0)} - T^{\dagger}d_T^{(1)} \qquad h = d_L^{(1)} - T^{\dagger}d_{T,L}^{(1,1)} \qquad (46a)$$

$$^{\infty}\Delta S = -d_T^{(1)} \qquad s = -d_{T,L}^{(1,1)} \qquad (46b)$$

$$\Delta C_p = -2T^{\dagger}d_T^{(2)} \qquad (46c)$$

Thermodynamic data calculated with eqns. 46a–c are listed in Table VII in the rows designated by P (for polynomials).

With the aid of the coefficients in Table VI, in eqn. 42, chemical potentials were calculated for every *n*-alkane in the experimental domain of 110–190°C for every 10 K interval. On these set of points, coefficients of eqn. 3 were calculated by non-linear regression. The regression coefficients are listed in Table VII in the rows designated by K (for Kirchhoff's approximation).

Finally, for dodecane and tridecane, thermodynamic functions were estimated as follows (retention data were not determined for these solutes in the whole temperature domain). First, values of h, s and ΔC_p (for tridecane also $^{\infty}\Delta H$) were calculated by linear extrapolation of the corresponding coefficients of $z = 9$, 10 and 11. These coefficients were fixed, then the remaining coefficients were calculated by non-linear regression of eqn. 3 on the experimental points. Values of these regression coefficients are given in Table VII in italics.

Solutes other than n-alkanes

Solutes were injected as mixtures and retention indices were calculated at the experimental column temperature T_{exp}. For each stationary liquid, the temperature dependence of the retention index was calculated with a linear regression. The retention indices $I(T_{\text{exp}})$ were then corrected for the small deviation δT from the nominal temperature with the aid of the slope to give retention indices at the nominal temperature $I(T_c)$. The resulting table was then considered as the basic experimental set for the following evaluations. The objective was to determine indices on all stationary liquids at every 20 K interval in the temperature domain 110–190°C. For solutes with high indices, values at lower temperatures were not determined (chromatogram times were too long).

In a first evaluation, the significant terms of eqn. 47 were elucidated by an analysis of variance.

$$I = \bar{I} + b_T^{(1)}P_T^{(1)} + b_T^{(2)}P_T^{(2)} + b_L^{(1)}P_L^{(1)} + b_L^{(2)}P_L^{(2)} + b_{T,L}^{(1,1)}P_T^{(1)}P_L^{(1)} \qquad (47)$$

where the symbols have analogous meanings to those in eqn. 32. Quadratic terms were hardly ever significant therefore $b_T^{(2)}$ and $b_L^{(2)}$ were considered to be equal zero. The variance corresponding to the mixed term was significant in most cases. In Table VIII,

TABLE VII

THERMODYNAMIC FUNCTIONS FOR THE TRANSFER OF 1 MOL OF *n*-ALKANE FROM THE IDEAL GAS STATE INTO 1 kg OF THE IDEAL DILUTE SOLUTION

P (for polynomial): calculated with the coefficients of eqn. 42 with the expressions given in eqns. 46. K (for Kirchhoff): calculated as the coefficients of eqn. 12 by non-linear regression on points generated by eqn. 42. The superscript $^{\infty}$ refers to a hypothetical liquid paraffin stationary phase of infinite molecular weight. Enthalpy and entropy are at the reference temperature $T^{\dagger} = 130.0 + 273.15$ K. For dodecane and tridecane values in parentheses are extrapolated and values in italics are calculated as explained in the text.

z	${}^{\infty}\Delta H_z$ (cal mol^{-1})	h_z (cal kg mol^{-2})	${}^{\infty}\Delta S_z$ (cal mol^{-1} K^{-1})	s_z (cal kg K^{-1} mol^{-2})	$\Delta C_{p,z}$ (cal mol^{-1} K^{-1})
5 P	−5558.6	+39.8	−16.4576	+0.463	+5.66
K	−5558.7	+39.8	−16.4581		+5.95
6 P	−6524.3	+32.4	−17.5407	+0.463	+7.36
K	−6524.4	+32.4	−17.5406		+7.73
7 P	−7504.3	+25.0	−18.6923	+0.463	+9.06
K	−7504.4	+25.0	−18.6927		+9.51
8 P	−8496.2	+17.6	−19.8961	+0.463	+10.76
K	−8496.2	+17.6	−19.8965		+11.30
9 P	−9496.1	+10.2	−21.1336	+0.463	+12.47
K	−9496.2	+10.1	−21.1340		+13.08
10 P	−10498.7	+2.7	−22.3868	+0.463	+14.17
K	−10498.6	+2.9	−22.3872		+14.86
11 P	−11497.2	−4.7	−23.6382	+0.463	+15.87
K	−11496.9	−4.6	−23.6382		+16.65
12 P	–	(−12.1)	–	(+0.463)	(+17.57)
K	*−12497.6*		*−24.8999*		(+18.43)
13 P	–	(−19.5)	–	(+0.463)	(+19.27)
K	−(13486.2)		*−26.1423*		(+20.21)

coefficients of eqn. 12, calculated from the coefficients of eqn. 47, are given for two variants. In the first variant only $b_T^{(1)}$ and $b_L^{(1)}$ were considered, resulting in a simplified form of eqn. 13 with $A_{T,\zeta} = 0$. In a second variant all significant coefficients were calculated.

In a second evaluation, the set of experimental retention indices were converted point for point by linear interpolation between two suitable *n*-alkanes following eqn. 14, where standard chemical potential differences of the *n*-alkanes were generated by eqn. 12 with the coefficients designated by K in Table VI. This set of data were submitted to an analysis of variance solute by solute with the following results. In most instances (over 95%), the term signalling the significance of s_j was significant and that corresponding to h_j was not. In applying eqn. 12 to the experimental data set, the following general behaviour was observed: (a) by putting $h_j = 0$ the coefficient s_j was significant; (b) by putting $s_j = 0$ the coefficient h_j was significant but the residual variance was higher than in case (a); (c) by allowing the existence of h_j and s_j simultaneously, neither of them was significant and the residual variance was highest.

From these observations, it was concluded that s_j and h_j were strongly correlated. This correlation will be discussed in the next section. Based on this correlation, it was considered to be sufficient to list only s_j in Table VII. The best combination of s_j and h_j is also indicated on a basis explained in the next section.

Table VIII also includes data for *n*-alkanes calculated as follows. With eqn. 3, a set of $\Delta\mu_z$ values were calculated for each *n*-alkane, by using coefficients listed in rows designated by K in Table VII. Eqn. 12 with $h_z \equiv 0$ was then fitted on this set by non-linear regression. The resulting coefficients, $s_z^{(0)}$ ($h_z = 0$), are also listed in Table VIII together with the standard deviation of this function around the generated points. It is observed that the resulting standard deviation is one order of magnitude smaller than the residual variance indicated in the analysis of variance in Table III, meaning that there is practically no difference in the description of $\Delta\mu_z$ of the *n*-alkanes by using the coefficients h_z *and* s_z or $s_z^{(0)}$ only.

RESULTS AND DISCUSSION

On the basis of the results of this study, it can be concluded that in the family of liquid paraffins as solvents, solutions at ideal dilution can be considered as equithermal if the heat of dissolution is calculated on a molal basis. In fact, if eqn. 12 is fitted to a data set, the smallest variance is observed if the coefficient responsible for the variation of the molal solution enthalpy, h_j, is put equal to zero with $s_j^{(0)}$ highly significant [the superscript (0) refers to "*s* only"]. If eqn. 12 with $s_j = 0$ is fitted, $h_j^{(1)}$ [the superscript (1) refers to "*h* only"] is highly significant but the residual variance is generally higher. Finally, if eqn. 12 with $s_j \neq 0$ and $h_j \neq 0$ is fitted, neither s_j nor h_j is significant and the residual variance is highest. This behaviour suggests that h_j and s_j are closely correlated. This relationship will be discussed later.

In summary, it is concluded that the dependence of the standard chemical potential difference of a solute on the inverse of the molecular weight of the stationary phase is best described by eqn. 5, with

$$R_j = -Ts_j^{(0)} \tag{48}$$

(*i.e.*, by eqn. 12 with $h_j = 0$) in the family of paraffinic solvents, B-x, of the structure shown in Fig. 1. Of course, the statement has to be considered as a result of the actual experimental design and with respect of the actual experimental error. The basis of the data is the set of chemical potentials of seven n-alkanes (pentane–undecane) on five stationary phases (B-59–B-103) at nine equidistant temperatures (110–190°C). The total error of a single determination was shown to be $\Delta_{95} = \pm 9.4$ cal mol^{-1}. The determination of the thermodynamic functions of solutes other than n-alkanes was based on retention indices, *i.e.*, on a scale relative to n-alkanes, and it is seen in Table VIII that the error of $\Delta\mu$ of these solutes is, in fact, always around $\Delta_{95} = \pm 9$ cal mol^{-1}.

The analysis of variance of the n-alkane data set shown in Table III seems to contradict the conclusion summarized in eqn. 48. In fact, the significant coefficients of eqn. 32 combine in a manner that in the final result both s_z and h_z are significant. This result is in contradiction to those found for all other solutes. Nevertheless, this description, admitted to be a best fit and eqn. 12 with the coefficients listed in Table VII, was used for the calculation of standard chemical potentials of all solutes from retention indices. On the other hand, it is observed that h_z changes from positive to negative with the carbon number, z, of the n-alkane solute, which is not logical, as it is highly improbable that the coefficient of the entropic variation would be independent of the size of these solutes. Therefore, the result was considered as a confusing artifact. In fact, the difference between the "s and h" and the "s only", $s^{(0)}$, variants is extremely slight. This is demonstrated on the example of n-alkanes by evaluating a data set generated with eqn. 12 and the coefficients listed under K in Table VII with the "s only" variant of eqn. 12. Data listed in Table VIII show that the standard deviation of the "s only" variant around points of the "s and h" variant is negligible (± 0.5 cal mol^{-1}) compared with the standard deviation of a single experiment (2nd residue in Table III; $\sigma = \pm 4.0$ cal mol^{-1}).

Consequence of the correlation of the coeffcients h and s

It is extremely unfortunate that no neat decision could be arrived at on the separate existence or non-existence of the enthalpic and entropic coefficients of variation. Actually, these coefficients are the necessary experimental data to correlate experimental results with results of model calculations.

It was already mentioned that these coefficients are probably strongly correlated. All our solutes have been evaluated by three variants of eqn. 12, "$h^{(1)}$ only", "$s^{(0)}$ only" and the "h and s" variant. In a first experiment, $h_j^{(1)}$ was plotted as a function of $-T^{\dagger}s^{(0)}$ shown in Fig. 3. The plot was linear and gave the following regression:

$$\varphi h_j^{(1)} = -T^{\dagger}s_j^{(0)} \tag{49}$$

with $\varphi = 0.9468 \pm 0.0068$. This result suggested that, in fact, in general, φh_j can compensate for any value of $-Ts_j$. A variable α_j was introduced in order to relate s_j to $s_j^{(0)}$ of a given solute j:

$$s_j = s_j^{(0)}(1 - \alpha_j) \tag{50}$$

implying $h_j = h_j^{(1)}\alpha_j$, and it was proposed that the relationship expressed in eqn. 51 is valid for any value of α_j for the residual function $\boldsymbol{R}_j$ (eqn. 9)

$$\boldsymbol{R}_j = -\frac{T^{\dagger}}{\varphi'}\alpha_j s_j^{(0)} - T(1 - \alpha_j)s_j^{(0)} \tag{51}$$

TABLE VIII

RETENTION INDICES AND THERMODYNAMIC DATA OF 124 CHOSEN SOLUTES IN A FAMILY OF BRANCHED HYDROCARBONS AS STATIONARY PHASES

Retention indices are described by eqn. 13. In the first line coefficients are listed with $A_{T,\zeta} = 0$, in the second line all significant coefficients are listed. Finally, retention indices on the C_{87} stationary liquid at 130°C, ${}^{87}I^{\dagger}$, are compared with those of ref. 18. Thermodynamic data were calculated by fitting eqn. 12 on the experimental points by putting $h_j = 0$ as explained in the text. In the first line the regression coefficients are listed, in the second line their standard deviation. Symbols: n is the number of points in the data set; σ is the standard deviation; all other symbols are as in the text.

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	${}^{\infty}I_{130}$	*10*A_T *(*K^{-1}*)*	A_ζ *(*mol^{-1} *kg)*	*10*$A_{T,\zeta}$ *(*$mol^{-1}K^{-1}$ *kg)*
HYDROCARBONS								
Alkanes								
00.05	Pentane	45	110–190	–	500.0	def		
00.06	Hexane	45	110–190	–	600.0	def		
00.07	Heptane	45	110–190	–	700.0	def		
00.08	Octane	45	110–190	–	800.0	def		
00.09	Nonane	45	110–190	–	900.0	def		
00.10	Decane	45	110–190	–	1000.0	def		
00.11	Undecane	45	110–190	–	1100.0	def		
00.12	Dodecane	45	110–190	–	1200.0	def		
00.13	Tridecane	45	110–190	–	1300.0	def		
Isoalkanes								
10.02	2,2-Dimethylbutane	25	110–190	1.13	539.9	0.75	+1.38	
				1.16	539.5	0.92	+1.74	−0.180
10.04	2,2-Dimethylpentane	25	110–190	0.70	625.5	0.56	+2.92	
				0.71	625.6	0.46	+2.72	+0.102
10.06	2,4-Dimethylpentane	25	110–190	0.98	625.9	0.17	+3.27	
				1.01	625.8	0.17	+3.28	−0.009
10.07	2,2,3-Trimethylbutane	25	110–190	0.92	651.6	1.56	+0.06	
				0.94	651.5	1.64	+0.23	−0.085
10.08	2,2-Dimethylhexane	25	110–190	0.79	716.0	0.52	+3.93	
				0.81	715.9	0.57	+4.02	−0.046
10.10	2,4-Dimethylhexane	25	110–190	0.54	730.9	0.37	+2.60	
				0.55	730.8	0.43	+2.72	−0.062
10.11	3,4-Dimethylhexane	25	110–190	0.51	782.0	1.09	−1.86	
				0.51	781.6	1.32	−1.37	−0.243
10.12	2,3,4-Trimethylpentane	25	110–190	0.78	765.9	1.47	−1.18	
				0.78	765.3	1.77	−0.55	−0.317
10.13	2,2,4-Trimethylpentane	25	110–190	0.59	691.3	0.88	+4.02	
				0.61	691.4	0.82	+3.88	+0.067
10.15	2,2,4,6,6-Pentamethylheptane	25	110–190	0.39	984.8	2.02	+6.64	
				0.40	984.7	2.03	+6.67	−0.013

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ *(cal mol^{-1})*	$^{\infty}\Delta S^{(0)}$ *(cal mol^{-1} K^{-1})*	ΔC_p *(cal mol^{-1} K^{-1})*	$s^{(0)}$ *(cal mol^{-2} K^{-1} kg)*	α	σ *(cal mol^{-1})*
		− 5521.1	−16.3695	5.94	0.3691	−0.25	0.52^a
		3.1	73	0.13	14		
		− 6493.8	−17.4685	7.73	0.3866	−0.20	0.42^a
		2.5	60	0.11	11		
		− 7480.7	−18.6372	9.51	0.4040	−0.15	0.33^a
		1.9	46	0.08	9		
		− 8479.6	−19.8574	11.30	0.4215	−0.10	0.23^a
		1.4	32	0.06	6		
		− 9486.5	−21.1114	13.08	0.4389	−0.05	0.13^a
		0.8	19	0.03	3		
		−10496.0	−22.3811	14.86	0.4563	−0.01	0.04^a
		0.2	5	0.01	1		
		−11501.3	−23.6486	16.65	0.4738	+0.02	0.06^a
		0.4	9	0.02	2		
		−12509.0	−24.9267	18.43	0.4912	+0.06	0.16^a
		0.9	22	0.04	4		
		−13481.6	−26.1336	20.21	0.5086	+0.09	0.26^a
		1.5	36	0.06	7		
541.0	541.2	−5746	−16.401	5.4	0.393	+0.09	5.7
540.9		34	80	1.4	15		
627.9	627.7	−6648	−17.521	7.4	0.426	−0.13	3.4
627.8		20	48	0.9	9		
628.6	629.5	−6746	−17.760	8.2	0.430	+0.01	4.8
628.5		29	68	1.2	13		
651.6	653.1	−6698	−17.317	8.5	0.397	−0.08	4.4
651.7		26	62	1.1	12		
719.2	719.6	−7594	−18.714	10.7	0.453	+0.12	3.6
719.2		22	51	0.9	10		
733.0	733.4	−7730	−18.865	9.4	0.440	+0.09	2.6
733.0		15	36	0.7	7		
780.5	780.4	−8072	−19.074	10.7	0.397	+0.06	2.3
780.5		14	33	0.6	6		
764.9	765.6	−7855	−18.740	11.0	0.402	+0.18	3.4
764.9		20	48	0.9	9		
694.6	694.8	−7239	−18.146	8.3	0.451	−0.01	2.9
694.6		17	41	0.7	8		
990.2	990.5	−9970	−21.279	11.9	0.530	+0.26	1.9
990.2		11	26	0.5	5		

(Continued on p. 160)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	$10A_T$ (K^{-1})	A_ζ $(mol^{-1}$ $kg)$	$10A_{T,\zeta}$ $(mol^{-1}K^{-1}$ $kg)$
10.16	2,6-Dimethyloctane	25	110–190	0.32	928.4	0.42	+2.96	
				0.32	928.2	0.50	+3.14	−0.090
1-Alkenes								
11.05	1-Pentene	25	110–190	1.41	485.6	0.24	−1.93	
				1.45	485.6	0.26	−1.91	−0.011
11.06	1-Hexene	25	110–190	0.84	587.8	0.21	−2.06	
				0.87	587.7	0.28	−1.91	−0.073
11.07	1-Heptene	25	110–190	0.58	686.9	0.20	−1.52	
				0.60	687.0	0.14	−1.63	+0.058
11.08	1-Octene	25	110–190	0.51	786.8	0.32	−1.75	
				0.52	786.5	0.48	−1.43	−0.159
11.09	1-Nonene	25	110–190	0.41	886.8	0.34	−1.54	
				0.40	886.5	0.51	−1.18	−0.178
11.10	1-Decene	25	110–190	0.42	986.8	0.31	−1.65	
				0.42	986.5	0.44	−1.37	−0.138
11.11	1-Undecene	20	150–190	0.56	1086.5	0.31	−1.24	
				0.57	1087.3	0.08	−2.15	+0.244
11.12	1-Dodecene	20	150–190	0.43	1186.3	0.26	−1.33	
				0.44	1185.9	0.37	−0.92	−0.109
1-Alkynes								
12.05	1-Pentyne	25	110–190	1.67	490.2	−0.09	−5.16	
				1.64	488.5	+0.76	−3.36	−0.899
12.06	1-Hexyne	25	110–190	1.18	594.1	−0.02	−5.24	
				1.15	592.9	+0.60	−3.94	−0.653
12.07	1-Heptyne	25	110–190	1.03	694.3	0.05	−4.86	
				1.00	693.1	0.63	−3.64	−0.611
12.08	1-Octyne	25	110–190	0.93	794.3	0.14	−4.92	
				0.91	793.3	0.62	−3.89	−0.517
12.09	1-Nonyne	25	110–190	0.89	895.6	0.13	−5.53	
				0.91	895.7	0.10	−5.59	+0.030
12.10	1-Decyne	25	110–190	0.98	995.0	0.31	−5.22	
				1.00	994.9	0.39	−5.07	−0.082
Monocyclic hydrocarbons								
13.05	Cyclopentane	20	130–190	1.80	598.3	1.51	−13.26	
				1.60	592.4	3.48	− 7.01	−2.083
13.06	Cyclohexane	20	130–190	1.93	700.7	3.03	−10.17	
				1.98	699.2	3.52	− 8.62	−0.516
13.07	Cycloheptane	40	110–190	0.63	848.5	4.20	−12.63	
				0.56	847.5	4.83	−11.55	−0.669
13.08	Cyclooctane	40	110–190	0.69	981.3	5.10	−17.30	
				0.45	978.8	6.15	−14.65	−1.117
13.10	Cyclodecane	19	130–190	1.02	1198.3	6.91	−22.14	
				0.92	1195.1	7.96	−18.79	−1.117

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ *(cal mol^{-1})*	$^{\infty}\Delta S^{(0)}$ *(cal mol^{-1} K^{-1})*	ΔC_p *(cal mol^{-1} K^{-1})*	$s^{(0)}$ *(cal mol^{-2} K^{-1} kg)*	α	σ *(cal mol^{-1})*
930.8	–	−9719	−21.336	13.4	0.478	+0.18	1.6
930.8		10	23	0.4	4		
484.0	483.9	−5329	−16.084	6.4	0.343	−0.38	7.3
484.0		43	103	1.8	19		
586.1	585.3	−6309	−17.171	7.1	0.359	−0.24	4.4
586.1		26	62	1.1	12		
685.7	685.2	−7279	−18.301	8.1	0.384	−0.32	2.9
685.7		17	41	0.7	8		
785.4	784.7	−8265	−19.494	10.8	0.399	−0.02	2.5
785.3		15	35	0.6	6		
885.5	885.0	−9270	−20.739	12.5	0.419	+0.05	1.9
885.5		12	27	0.5	5		
985.5	984.6	−10282	−22.014	14.2	0.435	+0.04	2.0
985.4		12	28	0.5	5		
1085.5	1084.3	−11243	−23.180	14.9	0.458	−0.27	2.6
1085.5		124	282	2.9	7		
1185.2	1184.3	−12232	−24.416	16.1	0.474	+0.10	2.0
1185.1		96	217	2.2	6		
486.0	484.9	−5417	−16.244	6.7	0.304	+0.84	8.4
485.8		50	118	2.1	22		
589.8	587.6	−6362	−17.221	5.9	0.321	+0.45	5.9
589.7		35	82	1.5	15		
690.3	688.4	−7338	−18.358	7.7	0.345	+0.39	4.9
690.1		29	69	1.2	13		
790.3	788.3	−8311	−19.514	9.1	0.363	+0.26	4.3
790.1		25	60	1.1	11		
891.1	888.0	−9336	−20.795	11.4	0.374	−0.48	4.4
891.1		26	62	1.1	12		
990.7	986.7	−10279	−21.905	11.5	0.396	−0.23	4.3
990.8		25	60	1.1	11		
587.5	588.3	−6031	−16.363	6.3	0.232	+2.88	8.6
586.7		134	309	4.2	25		
692.4	694.5	−6784	−16.917	7.4	0.292	−0.30	9.5
692.1		148	343	4.6	27		
838.2	838.8	−8005	−18.089	9.0	0.282	−0.09	2.6
838.1		12	31	0.6	5		
967.1	966.9	−9105	−19.185	9.3	0.261	+0.36	2.3
966.8		12	28	0.5	5		
1180.2	1180.0	−10740	−20.602	6.2	0.255	−0.01	3.1
1179.7		48	111	1.5	9		

(Continued on p. 162)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	$10A_T$ (K^{-1})	A_ζ $(mol^{-1}\ kg)$	$10A_{T,\zeta}$ $(mol^{-1}K^{-1}\ kg)$
Bicyclic hydrocarbons								
14.01	*cis*-Hydrindane	30	140–190	0.62	1055.2	5.68	−21.46	
				0.59	1053.0	6.33	−19.04	−0.690
14.02	*trans*-Hydrindane	30	140–190	0.71	1018.8	5.30	−18.79	
				0.67	1016.2	6.04	−16.05	−0.783
14.03	*cis*-Decalin	35	130–190	0.64	1174.6	7.13	−23.83	
				0.39	1170.7	8.42	−19.70	−1.372
14.04	*trans*-Decalin	40	120–190	0.63	1131.2	6.45	−21.13	
				0.46	1128.8	7.41	−18.59	−1.014
Alkylbenzenes								
15.00	Benzene	24	110–180	1.36	690.1	3.12	−16.90	
				1.22	687.3	4.47	−14.03	−1.435
15.01	Toluene	35	110–190	1.30	801.7	2.95	−19.29	
				1.10	798.2	4.34	−15.52	−1.469
15.02	Ethylbenzene	25	110–190	1.07	894.4	3.30	−19.83	
				0.83	891.9	4.53	−17.23	−1.302
15.03	Propylbenzene	25	110–190	0.98	981.8	3.57	−18.42	
				0.83	979.9	4.53	−16.38	−1.018
15.04	Butylbenzene	25	130–190	0.98	1081.4	3.58	−17.48	
				1.00	1081.5	3.54	−17.60	+0.040
15.05	Pentylbenzene	25	130–190	1.00	1176.9	3.75	−17.60	
				1.02	1176.8	3.78	−17.50	−0.034
Miscellaneous								
19.01	Adamantane	30	140–190	0.78	1159.8	8.28	−26.21	
				0.60	1154.6	9.77	−20.71	−1.571
19.03	Naphthalene	30	140–190	0.88	1249.5	7.82	−40.51	
				0.78	1245.1	9.06	−35.92	−1.311
19.04	Azulene	20	160–190	0.88	1371.4	8.89	−48.85	
				0.90	1370.1	9.15	−47.58	−0.281
ALKANE DERIVATIVES								
1-Chloroalkanes								
20.04	1-Chlorobutane	25	110–190	1.16	651.3	1.53	−10.46	
				1.15	650.3	2.03	− 9.40	−0.528
20.05	1-Chloropentane	25	110–190	1.06	754.6	1.67	−10.63	
				1.06	753.8	2.10	− 9.71	−0.460
20.06	1-Chlorohexane	25	110–190	1.08	856.0	1.80	−10.65	
				1.06	854.9	2.36	− 9.47	−0.588
20.07	1-Chloroheptane	25	110–190	1.09	957.2	1.88	−10.41	
				1.08	956.2	2.37	− 9.39	−0.510
Bromoalkanes								
21.02	Bromoethane	45	110–190	2.01	533.3	1.85	−12.93	
				2.03	534.0	1.51	−13.65	+0.361
21.03	1-Bromopropane	35	110–190	1.36	638.5	2.14	−12.36	
				1.29	636.2	3.05	− 9.88	−0.962

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ (*cal mol*$^{-1}$)	$^{\infty}\Delta S^{(0)}$ (*cal mol*$^{-1}$ *K*$^{-1}$)	ΔC_p (*cal mol*$^{-1}$ *K*$^{-1}$)	$s^{(0)}$ (*cal mol*$^{-2}$ *K*$^{-1}$ *kg*)	α	σ (*cal mol*$^{-1}$)
1037.6	1034.9	−9844	−20.116	14.2	0.241	−0.77	2.5
1037.4		60	137	1.6	6		
1003.4	1000.3	−9617	−19.992	15.0	0.263	−0.36	2.7
1003.1		65	148	1.8	6		
1155.1	1153.9	−10580	−20.491	10.3	0.232	+0.36	1.8
1154.6		25	57	0.8	4		
1113.9	1112.2	−10345	−20.427	11.8	0.248	−0.11	2.1
1113.6		17	39	0.6	4		
676.3	678.8	−6634	−16.687	11.0	0.201	+1.27	5.4
675.8		31	74	1.7	13		
785.9	786.5	−7733	−18.012	9.8	0.204	+0.96	4.9
785.5		27	63	1.1	11		
878.2	875.9	−8568	−18.926	9.7	0.210	+0.55	4.1
877.8		24	57	1.0	11		
966.7	965.0	−9372	−19.835	8.8	0.244	+0.09	3.7
966.5		22	52	0.9	10		
1067.1	1064.8	−10394	−21.158	11.5	0.282	−1.45	4.8
1067.1		67	154	2.0	12		
1162.5	1162.0	−11291	−22.218	12.0	0.298	−1.23	4.8
1162.5		65	151	2.0	12		
1138.4	1137.6	−10285	−19.942	12.1	0.211	+0.55	2.7
1137.7		64	145	1.7	6		
1216.4	1215.4	−11067	−20.823	11.7	0.078	−3.34	3.6
1215.7		86	195	2.3	8		
1331.4	1331.2	−11994	−21.685	13.5	0.034	—	4.4
1331.2		423	943	8.9	12		
642.7	641.4	−6548	−16.955	5.5	0.271	−0.18	5.7
642.6		34	80	1.4	15		
745.9	743.3	−7543	−18.114	6.8	0.290	−0.26	5.0
745.9		30	71	1.3	13		
847.3	844.8	−8533	−19.303	8.4	0.309	0.00	4.9
847.2		29	70	1.2	13		
948.7	946.3	−9539	−20.545	10.0	0.330	−0.05	4.9
948.5		29	69	1.2	13		
522.7	523.0	−5301	−15.398	3.5	0.217	−2.72	10.7
522.8		54	127	2.3	21		
628.4	629.4	−6273	−16.444	4.6	0.251	+0.50	6.0
628.1		32	77	1.4	13		

(Continued on p. 164)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	$10A_T$ (K^{-1})	A_{ζ} $(mol^{-1}\ kg)$	$10A_{T,\zeta}$ $(mol^{-1}K^{-1}\ kg)$
21.04	1-Bromobutane	35	110–190	1.18	742.0	2.39	−11.59	
				1.10	739.8	3.31	− 9.10	−0.968
21.05	1-Bromopentane	40	110–190	0.95	845.3	2.62	−12.20	
				0.85	843.1	3.54	− 9.88	−0.976
21.06	1-Bromohexane	40	110–190	0.62	946.4	2.89	−12.13	
				0.54	944.9	3.52	−10.55	−0.667
21.07	1-Bromoheptane	45	110–190	0.64	1048.3	3.06	−12.78	
				0.59	1047.4	3.54	−11.76	−0.509
1-Iodoalkanes								
22.01	Iodomethane	25	110–190	1.10	565.8	3.09	−18.88	
				1.10	564.9	3.54	−17.92	−0.484
22.02	Iodoethane	25	110–190	1.01	654.9	3.34	−17.38	
				1.01	654.2	3.69	−16.63	−0.377
22.03	1-Iodopropane	25	110–190	1.11	761.5	3.77	−19.11	
				0.95	759.5	4.81	−16.91	−1.098
22.04	1-Iodobutane	25	110–190	1.18	862.9	3.94	−19.26	
				0.98	860.5	5.15	−16.72	−1.272
22.05	1-Iodopentane	25	110–190	1.22	963.6	4.07	−19.26	
				1.06	961.3	5.20	−16.85	−1.205
1-Cyanoalkanes								
23.03	1-Cyanoethane	40	110–190	4.13	496.1	0.84	− 7.78	
				4.17	495.0	1.40	− 6.67	−0.591
23.04	1-Cyanopropane	40	110–190	1.49	594.0	1.21	− 6.17	
				1.50	593.4	1.47	− 5.52	−0.274
23.05	1-Cyanobutane	40	110–190	0.93	701.9	1.47	− 7.82	
				0.89	700.4	2.09	− 6.25	−0.657
23.06	1-Cyanopentane	45	110–190	0.69	804.4	1.71	− 8.12	
				0.62	803.1	2.36	− 6.75	−0.686
23.07	1-Cyanohexane	25	110–190	2.52	921.6	1.57	−15.70	
				2.57	921.3	1.92	−14.95	−0.374
23.08	1-Cyanoheptane	25	110–190	2.89	1020.8	1.95	−13.93	
				2.94	1019.8	2.46	−12.85	−0.541
1-Nitroalkanes								
24.01	Nitromethane	25	110–170	3.57	467.3	0.96	−10.07	
				3.34	462.7	4.28	− 5.15	−3.511
24.02	Nitroethane	30	110–190	2.70	577.2	1.16	−12.85	
				2.61	573.7	2.74	− 9.18	−1.682
24.03	1-Nitropropane	30	110–190	1.60	672.0	1.62	−10.87	
				1.60	670.8	2.17	− 9.61	−0.582
24.04	1-Nitrobutane	30	110–190	1.03	777.2	1.87	−11.71	
				1.01	776.0	2.41	−10.46	−0.577
24.05	1-Nitropentane	45	110–190	0.58	877.3	2.31	−10.50	
				0.46	875.9	3.04	− 8.97	−0.767
24.06	1-Nitrohexane	45	110–190	0.53	978.6	2.49	−10.69	
				0.36	977.1	3.25	− 9.08	−0.806

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ *(cal mol⁻¹)*	$^{\infty}\Delta S^{(0)}$ *(cal mol⁻¹ K⁻¹)*	ΔC_p *(cal mol⁻¹ K⁻¹)*	$s^{(0)}$ *(cal mol⁻² K⁻¹ kg)*	α	σ *(cal mol⁻¹)*
732.5	732.7	−7258	−17.571	5.9	0.281	+0.48	5.0
732.4		27	64	1.2	11		
835.3	835.0	−8263	−18.772	8.4	0.292	+0.47	4.0
835.0		21	50	0.9	8		
936.5	936.4	−9254	−19.978	11.1	0.312	+0.04	2.7
936.3		14	34	0.6	6		
1037.8	1036.2	−10246	−21.182	12.8	0.321	−0.24	2.9
1037.8		15	35	0.6	6		
550.4	548.8	−5294	−14.960	3.1	0.149	−1.83	5.9
550.2		35	83	1.5	16		
640.7	638.9	−6149	−15.927	4.4	0.189	−1.54	5.5
640.6		32	77	1.4	14		
745.9	743.8	−7102	−16.943	5.2	0.193	+0.16	4.6
745.7		27	65	1.2	12		
847.1	844.6	−8087	−18.120	6.6	0.212	+0.56	4.7
846.8		28	66	1.2	12		
947.8	944.6	−9079	−19.334	8.1	0.229	+0.33	4.7
947.5		28	65	1.2	12		
489.7	—	−5253	−15.765	6.3	0.272	+0.05	21.2
489.5		114	270	4.9	44		
589.0	593.6	−6097	−16.571	5.5	0.312	−0.22	7.5
588.9		40	95	1.6	16		
695.5	697.4	−7133	−17.762	8.8	0.315	+0.26	4.3
695.3		23	55	1.0	9		
797.8	799.1	−8095	−18.859	9.7	0.329	+0.26	3.0
797.6		15	36	0.6	6		
908.8	899.7	−9137	−19.984	6.4	0.263	−0.76	11.6
909.1		69	164	2.9	30		
1009.4	1001.3	−10008	−20.921	4.3	0.302	−0.14	12.2
1009.3		73	172	3.1	32		
459.1	—	−4975	−15.458	12.4	0.234	+6.30	17.9
458.5		108	255	8.2	48		
566.7	578.6	−5924	−16.371	7.3	0.226	+2.12	13.2
566.2		72	171	3.1	32		
663.1	665.1	−6783	−17.277	8.6	0.271	−0.10	7.7
662.9		42	99	1.8	18		
767.6	767.2	−7797	−18.465	11.2	0.282	−0.16	4.4
767.4		24	57	1.0	11		
868.7	868.8	−8682	−19.410	10.2	0.314	+0.28	2.2
868.6		11	27	0.5	4		
969.9	969.9	−9674	−20.618	12.0	0.331	+0.35	1.8
969.7		9	22	0.4	4		

(Continued on p. 166)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	*10A*$_T$ *(K*$^{-1}$*)*	*A*$_\zeta$ *(mol*$^{-1}$ *kg)*	*10A*$_{T,\zeta}$ *(mol*$^{-1}$*K*$^{-1}$ *kg)*
1-Acetoxyalkanes								
25.02	1-Acetoxyethane	25	110–190	1.74	555.6	−1.05	−10.91	
				1.46	552.1	+0.71	−7.19	−1.863
25.03	1-Acetoxypropane	25	110–190	1.41	650.4	−0.76	−7.19	
				1.36	648.8	+0.06	−5.46	−0.866
25.04	1-Acetoxybutane	25	110–190	1.46	751.8	−0.63	−6.87	
				1.42	750.2	+0.17	−5.18	−0.844
25.05	1-Acetoxypentane	25	110–190	1.54	851.5	−0.54	−6.20	
				1.52	850.0	+0.17	−4.69	−0.758
25.06	1-Acetoxyhexane	25	110–190	1.56	949.9	−0.46	−5.31	
				1.57	948.9	+0.04	−4.26	−0.528
1-Alkanols								
31.03	1-Propanol	30	110–190	3.91	501.2	0.83	−11.60	
				3.98	501.7	0.54	−12.17	+0.311
31.04	1-Butanol	45	110–190	4.83	611.6	1.17	−14.95	
				4.73	607.2	3.51	−10.02	−2.468
31.05	1-Pentanol	45	110–190	3.17	715.0	1.24	−14.24	
				3.12	712.4	2.65	−11.27	−1.486
31.06	1-Hexanol	40	110–190	2.07	814.8	1.30	−12.65	
				2.08	813.3	1.97	−10.97	−0.708
31.07	1-Heptanol	40	110–190	1.95	916.2	1.38	−12.33	
				1.92	913.9	2.34	−9.91	−1.020
31.08	1-Octanol	40	110–190	1.94	1019.2	1.52	−14.46	
				1.94	1017.5	2.24	−12.68	−0.754
2-Alkanols								
32.04	2-Butanol	24	110–190	1.68	571.9	0.59	−17.56	
				1.72	572.1	0.46	−17.84	+0.139
32.05	2-Pentanol	24	110–190	1.57	668.6	0.44	−14.86	
				1.60	668.8	0.33	−15.10	+0.119
32.06	2-Hexanol	24	110–190	1.38	768.3	0.32	−14.18	
				1.41	768.7	0.11	−14.62	+0.221
32.07	2-Heptanol	24	110–190	1.43	868.2	0.29	−13.77	
				1.46	868.6	0.10	−14.18	+0.201
2-Methyl-2-alkanols								
33.05	2-Methyl-2-butanol	25	110–190	2.09	617.2	0.54	−12.03	
				2.14	617.3	0.50	−12.11	+0.039
33.06	2-Methyl-2-pentanol	25	110–190	1.78	707.6	0.52	−9.88	
				1.81	707.4	0.60	−9.72	−0.081
33.07	2-Methyl-2-hexanol	25	110–190	1.79	802.8	0.51	−9.42	
				1.84	802.5	0.66	−9.10	−0.158
33.08	2-Methyl-2-heptanol	25	110–190	1.97	900.7	0.47	−9.10	
				2.02	900.9	0.37	−9.30	+0.099

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ *(cal mol^{-1})*	$^{\infty}\Delta S^{(0)}$ *(cal mol^{-1} K^{-1})*	ΔC_p *(cal mol^{-1} K^{-1})*	$s^{(0)}$ *(cal mol^{-2} K^{-1} kg)*	α	σ *(cal mol^{-1})*
546.7	544.0	−6140	−17.180	5.0	0.244	+2.59	8.0
546.2		48	112	2.0	21		
644.5	638.9	−7048	−18.201	7.2	0.309	+0.68	6.8
644.3		41	96	1.7	18		
746.2	740.9	−8003	−19.286	7.8	0.332	+0.64	6.7
746.0		40	94	1.7	18		
846.4	841.1	−8982	−20.464	9.0	0.358	+0.55	6.9
846.2		41	97	1.8	18		
945.6	939.4	−9960	−21.671	10.5	0.386	+0.32	7.0
945.4		42	99	1.8	18		
491.7	–	−5351	−15.945	10.3	0.226	−2.20	20.9
491.7		120	283	4.8	50		
599.4	600.9	−6165	−16.518	3.9	0.209	+3.84	23.9
599.0		120	283	5.1	47		
703.4	701.9	−7225	−17.828	7.7	0.240	+1.31	15.1
703.2		76	179	3.3	30		
804.5	803.6	−8192	−18.975	7.6	0.282	+0.07	9.7
804.3		52	122	2.1	20		
906.1	905.6	−9220	−20.265	10.3	0.304	+0.70	9.1
905.8		49	114	2.0	19		
1007.4	1006.6	−10196	−21.417	11.2	0.299	+0.10	8.8
1007.1		47	110	1.9	18		
557.5	552.0	−5970	−16.559	8.5	0.166	−3.31	8.8
557.5		52	124	2.2	23		
656.4	648.2	−6970	−17.789	10.0	0.221	−2.11	8.0
656.4		48	112	2.0	21		
756.7	748.0	−7962	−18.986	10.2	0.250	−1.96	7.2
756.7		43	101	1.8	19		
856.9	848.0	−8953	−20.197	10.9	0.274	−1.64	7.2
857.0		43	101	1.8	19		
607.4	600.9	−6413	−17.059	6.0	0.246	−1.52	11.4
607.4		68	160	2.9	30		
699.5	693.8	−7292	−18.079	5.8	0.289	−0.85	9.0
699.4		54	127	2.3	24		
795.1	788.3	−8237	−19.225	6.8	0.312	−0.58	8.9
795.1		53	125	2.2	23		
893.3	885.8	−9230	−20.470	8.2	0.334	−0.83	9.6
893.3		57	135	2.4	25		

(Continued on p. 168)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	$10A_T$ (K^{-1})	A_ζ $(mol^{-1}\ kg)$	$10A_{T,\zeta}$ $(mol^{-1}K^{-1}\ kg)$
2-Alkanones								
40.04	2-Butanone	30	110–180	3.63	543.3	0.66	− 9.96	
				3.53	538.7	2.97	− 5.09	−2.439
40.05	2-Pentanone	36	110–180	2.19	636.2	0.73	− 9.19	
				2.09	633.0	2.33	− 5.80	−1.694
40.06	2-Hexanone	30	110–180	1.45	737.2	0.77	− 6.84	
				1.39	735.2	1.80	− 4.67	−1.086
40.07	2-Heptanone	30	110–180	0.87	838.2	0.76	− 6.68	
				0.77	836.2	1.65	− 4.81	−0.937
40.08	2-Octanone	45	110–190	0.67	937.7	1.01	− 6.25	
				0.58	936.3	1.71	− 4.76	−0.748
40.09	2-Nonanone	45	110–190	0.61	1038.0	1.08	− 6.43	
				0.54	1036.9	1.64	− 5.24	−0.594
Ethers								
41.06	Dipropyl ether	25	110–190	0.94	658.6	−0.27	− 1.20	
				0.96	658.5	−0.19	− 1.04	−0.080
41.08	Dibutyl ether	25	110–190	0.69	856.2	−0.15	− 0.31	
				0.70	856.0	−0.04	− 0.10	−0.109
41.10	Dipentyl ether	25	110–190	0.68	1052.2	0.08	+ 0.44	
				0.69	1051.9	0.23	+ 0.76	−0.163
Halogenomethanes								
42.22	Dichloromethane	30	110–180	2.91	518.2	2.08	−15.46	
				2.52	511.8	5.29	− 8.66	−3.400
42.23	Trichloromethane	30	110–180	1.90	616.8	−2.46	−12.46	
				1.88	614.8	3.46	−10.33	−1.064
42.24	Tetrachloromethane	40	110–190	0.83	688.5	2.83	− 9.16	
				0.84	688.5	2.85	− 9.12	−0.019
42.32	Dibromomethane	25	110–190	2.20	733.9	3.95	−27.40	
				1.98	730.3	5.78	−23.53	−1.933
42.33	Tribromomethane	25	110–190	2.87	942.7	6.05	−29.63	
				2.94	942.9	5.96	−29.83	+0.102
HALOGENOBENZENES								
50.11	Fluorobenzene	25	110–190	1.65	684.0	2.27	−17.71	
				1.52	681.4	3.53	−15.04	−1.335
50.21	Chlorobenzene	35	110–190	0.79	884.6	4.32	−22.33	
				0.52	881.6	5.48	−19.18	−1.226
50.31	Bromobenzene	40	110–190	0.74	983.8	5.52	−26.63	
				0.56	981.5	6.51	−24.13	−1.052
50.41	Iodobenzene	25	130–190	1.52	1115.7	6.90	−35.74	
				1.56	1115.1	7.07	−35.20	−0.181
PYRIDINES								
60.01	Pyridine	25	110–190	1.79	749.9	3.77	−26.90	
				1.67	747.3	5.07	−24.17	−1.370

		Thermodynamic data					
$^{87}I_{130}$	*Ref. (11)*	$^{\infty}\Delta H^{(0)}$ *(cal mol^{-1})*	$^{\infty}\Delta S^{(0)}$ *(cal mol^{-1} K^{-1})*	ΔC_p *(cal mol^{-1} K^{-1})*	$s^{(0)}$ *(cal mol^{-2} K^{-1} kg)*	α	σ *(cal mol^{-1})*
535.2	543.5	−5831	−16.587	14.8	0.254	+3.61	17.3
534.5		100	236	5.5	41		
628.7	632.2	−6696	−17.523	13.5	0.283	+1.99	9.8
628.3		57	134	3.1	24		
731.6	733.7	−7704	−18.734	14.7	0.331	+0.96	5.9
731.4		34	80	1.9	14		
832.7	833.4	−8675	−19.880	13.5	0.351	+0.74	3.5
832.3		20	48	1.1	8		
932.6	933.2	−9599	−20.931	12.5	0.374	+0.50	3.0
932.4		15	35	0.6	6		
1032.7	1033.4	−10593	−22.161	14.0	0.390	+0.31	2.7
1032.6		14	32	0.6	5		
657.6	655.2	−7109	−18.246	8.5	0.382	−0.14	4.7
657.6		28	66	1.2	12		
855.9	855.1	−9049	−20.570	11.2	0.428	+0.03	3.3
855.9		20	46	0.8	9		
1052.6	1053.0	−10977	−22.931	14.0	0.470	+0.20	3.0
1052.5		18	42	0.8	8		
505.6	509.1	−5174	−15.289	9.1	0.182	+7.11	13.7
504.7		79	187	4.4	33		
606.6	610.3	−6075	−16.230	9.5	0.240	+0.48	8.9
606.3		51	121	2.8	21		
681.0	681.8	−6676	−16.795	6.2	0.291	−0.95	4.3
681.0		22	52	1.0	9		
711.5	706.2	−6643	−16.154	0.9	0.090	+2.40	9.0
711.1		54	127	2.3	24		
918.5	912.9	−8328	−17.738	3.6	0.109	−7.30	15.1
918.5		90	212	3.8	40		
669.5	665.9	−6603	−16.679	3.0	0.190	+0.94	7.0
669.1		42	98	1.8	18		
866.3	866.1	−8228	−18.214	8.1	0.187	+0.23	2.5
865.9		14	32	0.6	6		
962.0	961.1	−8956	−18.796	8.9	0.156	−0.91	2.9
961.8		15	36	0.6	6		
1086.5	1081.1	−9892	−19.526	8.6	0.092	−8.03	7.9
1086.3		106	250	3.3	20		
727.9	728.3	−6948	−16.717	6.7	0.100	−0.15	8.2
727.5		49	115	2.1	21		

(Continued on p. 170)

TABLE VIII *(continued)*

No.	*Compound*	*n*	*Temperature range (°C)*	*Retention index*				
				σ	$^{\infty}I_{130}$	$10A_T$ (K^{-1})	A_{ζ} $(mol^{-1}\ kg)$	$10A_{T,\zeta}$ $(mol^{-1}K^{-1}\ kg)$
SILICANE DERIVATIVES								
70.01	Tetramethylsilane	30	110–170	1.96	419.8	−0.57	+ 7.32	
				1.97	420.3	−1.28	+ 6.82	+0.748
70.02	Hexamethyldisilane	25	110–190	1.61	672.1	+0.11	+16.66	
				1.64	672.5	−0.10	+16.23	+0.212
70.03	1,2-Bis(trimethylsilyl)ethane	25	110–190	0.48	815.7	−0.94	+20.57	
				0.47	816.2	−1.21	+20.00	+0.281
70.04	Hexamethyldisiloxane	25	110–190	0.86	576.2	−2.46	+24.53	
				0.84	577.1	−2.90	+23.61	+0.460
70.05	Hexamethylcyclotrisiloxane	25	110–190	0.92	687.9	−3.21	+27.21	
				0.82	689.5	−3.99	+25.54	+0.832
MISCELLANEOUS								
90.01	Tetrahydrofuran	25	110–190	2.21	631.9	1.70	−19.43	
				2.25	631.0	2.16	−18.47	−0.478
90.02	1,4-Dioxane	25	110–190	2.07	693.3	2.15	−19.99	
				2.10	692.4	2.58	−19.08	−0.458

[a] Standard deviation of the regression with $h = 0$ relative to points generated by eqn. 42.

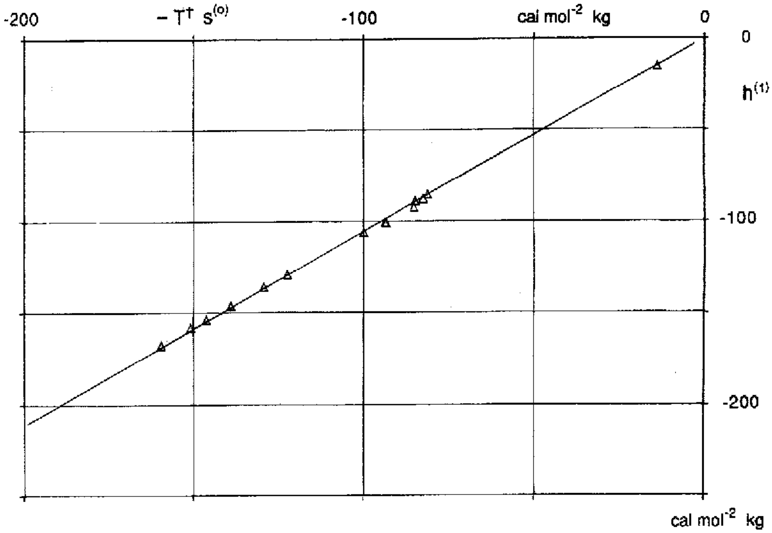

Fig. 3. Correlation of the regression coefficients $h_j^{(1)}$ ("h only") and $s_j^{(0)}$ ("s only") as special cases of eqn. 9: plot of $h_j^{(1)}$ as a function of $T^{\dagger}s_j^{(0)}$ (see eqn. 49).

		Thermodynamic data					
${}^{87}I_{130}$	*Ref. (11)*	${}^{\infty}\Delta H^{(0)}$ *(cal mol⁻¹)*	${}^{\infty}\Delta S^{(0)}$ *(cal mol⁻¹ K⁻¹)*	ΔC_p *(cal mol⁻¹ K⁻¹)*	$s^{(0)}$ *(cal mol⁻² K⁻¹ kg)*	α	σ *(cal mol⁻¹)*
425.8	427.1	−4866	−15.788	−1.7	0.447	−0.79	9.9
425.9		57	134	4.0	25		
685.7	–	−7331	−18.606	8.8	0.598	+0.33	8.5
685.8		51	120	2.2	22		
832.5	–	−9029	−21.004	13.0	0.662	+0.46	2.8
832.6		17	40	0.7	7		
596.3	–	−7041	−19.114	11.0	0.681	+0.31	4.3
596.4		25	60	1.1	11		
710.2	–	−8286	−20.761	12.8	0.721	+0.20	4.1
710.4		24	57	1.0	11		
616.0	612.9	−6230	−16.423	4.5	0.161	−1.72	11.2
615.9		67	158	2.8	30		
676.9	675.0	−6708	−16.822	3.6	0.165	−1.76	10.3
676.8		61	145	2.6	27		

In order to test eqn. 51 at $T = T^{\dagger}$, experimental values of $h_{j,\text{exp}}$, $s_{j,\text{exp}}$ and $s_{j,\text{exp}}^{(0)}$ were used in

$$y = \frac{h_{j,\text{exp}} - T^{\dagger} s_{j,\text{exp}}}{-T^{\dagger} s_{j,\text{exp}}^{(0)}} = \frac{\alpha_{j,\text{exp}}}{\varphi'} + (1 - \alpha_{j,\text{exp}}) \tag{52}$$

The value of $\alpha_{j,\text{exp}}$ was calculated with eqn. 50 by using experimental regression data:

$$\alpha_{j,\text{exp}} = 1 - [s_{j,\text{exp}}/s_{j,\text{exp}}^{(0)}] \tag{53}$$

The plot of the left-hand side of eqn. 52 as a function of $\alpha_{j,\text{exp}}$ is shown in Fig. 4. The correlation is excellent, with a value of $\varphi' = 0.9465 \pm 0.0037$.

If the equations were evaluated with different combinations of s_j and h_j, the values of ${}^{\infty}\Delta H_j$ and ${}^{\infty}\Delta S_j$ were also different, but $\Delta C_{p,j}$ remained constant. In Fig. 5, the difference ${}^{\infty}\Delta H_j - {}^{\infty}\Delta H_j^{(0)}$ is plotted as a function of $h_{j,\text{exp}}$. It gave the following correlation:

$${}^{\infty}\Delta H_{j,\text{exp}} = {}^{\infty}\Delta H_{j,\text{exp}}^{(0)} - \varphi'' h_{j,\text{exp}} \tag{54}$$

with $\varphi'' = 0.9451 \pm 0.0002$. In Fig. 6, the difference $T[{}^{\infty}\Delta S_j - {}^{\infty}\Delta S_j^{(0)}]$ is plotted as a function of $-T^{\dagger}[s_{j,\text{exp}}^{(0)} - s_{j,\text{exp}}]$. The following correlation is valid:

$${}^{\infty}\Delta S_{j,\text{exp}} = {}^{\infty}\Delta S_{j,\text{exp}}^{(0)} - \varphi'''[s_{j,\text{exp}} - s_{j,\text{exp}}^{(0)}] \tag{55}$$

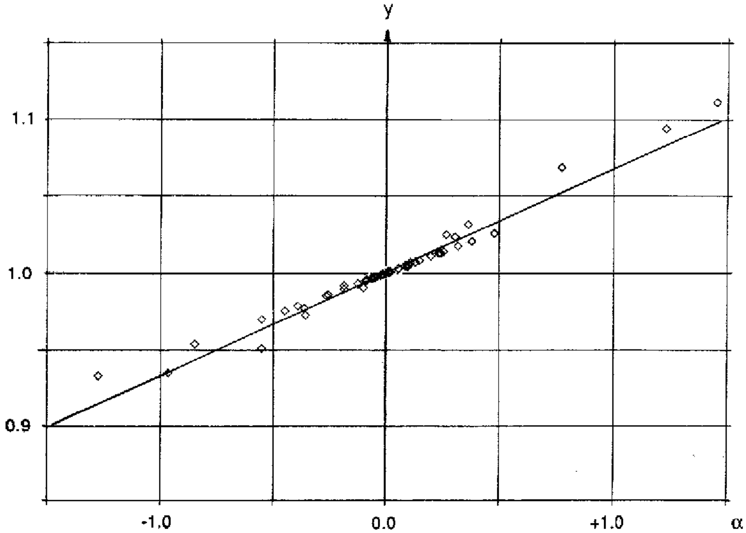

Fig. 4. Plot of the combination of experimental regression coefficients $h_{j,\mathrm{exp}}$ and $s_{j,\mathrm{exp}}$ as a function of $\alpha_{j,\mathrm{exp}}$ calculated with regression coefficients $s_{j,\mathrm{exp}}$ and $s^{(0)}_{j,\mathrm{exp}}$ as indicated in eqns. 52 and 53 (y in the left-hand side of eqn. 52).

with $\varphi''' = 0.9450 \pm 0.0001$. The factor $\varphi' = \varphi'' = \varphi'''$ is obviously the average of the ζ_L characterizing the five stationary phases, $\bar{\zeta} = 0.9450$ mol kg^{-1}.

Comparison of eqn. 51 with eqn. 9 resulted in eqns. 56 and 57. Substitution of these results in eqns. 54 and 55 gives the following set of four equations for the

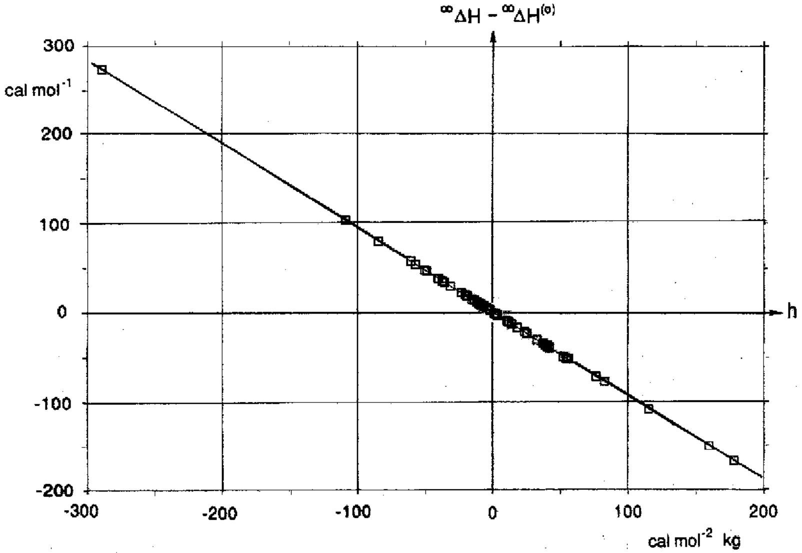

Fig. 5. Plot of the difference of experimental regression coefficients $^{\infty}\Delta H_{j,\mathrm{exp}} - {}^{\infty}\Delta H^{(0)}_{j,\mathrm{exp}}$ as a function of $h_{j,\mathrm{exp}}$ (see eqn. 54).

calculation of s_j, h_j, ${}^{\infty}\Delta H_j$ and ${}^{\infty}\Delta S_j$ for a given value of α from the data listed in Table VIII for $\alpha = 0$.

$$ {}^{\infty}\Delta H_j = {}^{\infty}\Delta H_j^{(0)} + T^{\dagger}\alpha_j s^{(0)} = {}^{\infty}\Delta H_j^{(0)} + 403.2\ \alpha_j s_j^{(0)} \qquad \text{cal mol}^{-1} \qquad (56)$$

$$ {}^{\infty}\Delta S_j = {}^{\infty}\Delta S_j^{(0)} + \bar{\zeta}\alpha_j s_j^{(0)} = {}^{\infty}\Delta S_j^{(0)} + 0.9450\ \alpha_j s_j^{(0)} \qquad \text{cal mol}^{-1}\ \text{K}^{-1} \qquad (57)$$

$$ h_j = -\frac{T^{\dagger}}{\bar{\zeta}}\alpha_j s_j^{(0)} = -426.6\ \alpha_j s_j^{(0)} \qquad \text{cal mol}^{-2}\ \text{kg} \qquad (58)$$

$$ s_j = (1 - \alpha_j) s_j^{(0)} \qquad \text{cal mol}^{-2}\ \text{K}^{-1}\ \text{kg} \qquad (59)$$

It should be noted that the relationships summarized in eqns. 56–59 are not valid mathematically. They are good approximations in a restricted range of α, estimated roughly as $\alpha_j = -2$ to $+2$.

In conclusion, the statement summarized in eqn. 48, *i.e.*, the variant "$s^{(0)}$ only", is the best statistically significant variant of eqn. 12; it can be extended as follows. Any model which results in a linear combination of h_j and s_j satisfying eqn. 51 is justified from a statistical viewpoint if the value of α does not exceed ± 2. In fact, for such a linear combination, the residual variance around the regression of eqn. 12 remain almost the same as for the "$s^{(0)}$ only" variant.

In Table VIII, the thermodynamic functions listed are related to the "$s^{(0)}$ only" variant ($\alpha = 0$). Also is given for each solute the value of α_j corresponding to the best combination of h_j and s_j as revealed by fitting eqn. 12 to experimental data.

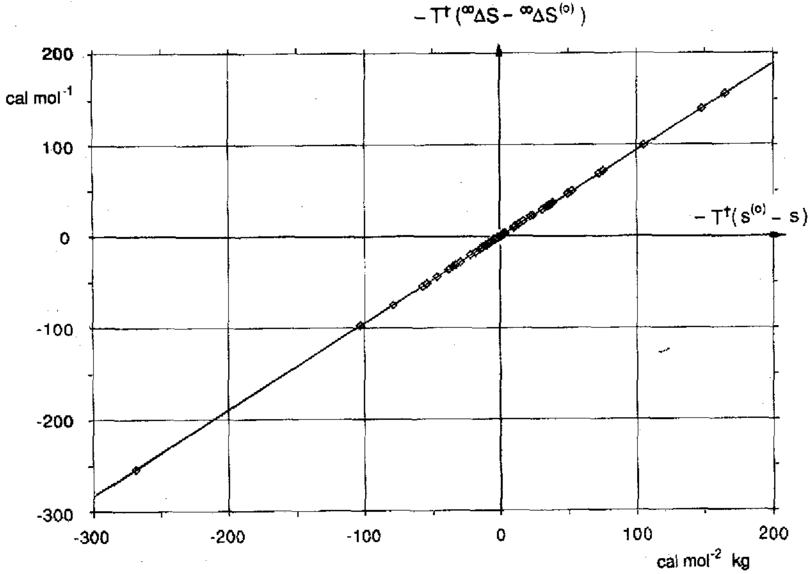

Fig. 6. Plot of the difference of experimental regression coefficients ${}^{\infty}\Delta S_{j,\text{exp}} - {}^{\infty}\Delta S_{j,\text{exp}}^{(0)}$ as a function of the difference $s_{j,\text{exp}} - s_{j,\text{exp}}^{(0)}$ (see eqn. 55).

Standard chemical potential differences with other reference states

It is obvious that standard chemical potential differences referring to different reference states are related to each other by simple mathematical rules; consequently, they do not give new information about solution behaviour. However, it frequently happens that correlations between molecular properties and solution behaviour are simpler to explain in another language. Arguments were already given in favour of chemical potential related to the molal Henry coefficient, g_j[1,2]. Arguments against the chemical potential related to the Henry coefficient, h_j^*, are numerous. This function becomes $-\infty$ for $\zeta \rightarrow 0$ and solution data expressed as $\Delta\mu_j^{(h^*)}$ will have a strong dependence on the variable ζ by the nature of the definition of h_j^* (see eqns. 20 and 24).

Solution data have already been discussed in terms of $\Delta\mu^{(D)}$, *i.e.*, chemical potentials related to the distribution coefficient, K_D, as defined in eqn. 22 [10]. Therefore, conversion of our data to $\Delta\mu_j^{(D)}$ will be discussed, and two methods will be given.

Combination of eqns. 20, 1 and 22 gives the relationship between $\Delta\mu$ (related to g) and $\Delta\mu^{(D)}$.

$$\Delta\mu - \Delta\mu^{(D)} = RT \ln (\mathcal{R}T\rho_L) \tag{60}$$

where the density of the stationary liquid, ρ_L, is given in eqn. 10 (for coefficients of eqn. 10, see Table I). Substitution of eqn. 10 in eqn. 60 with suitable numerical values of the coefficients gives

$$\begin{aligned} \Delta\mu - \Delta\mu^{(D)} = & -4.874\ T + 1.987 T \ln T - 13.91 \cdot 10^{-4}\ T^2 \\ & - 0.057\ T\zeta + 2.03 \cdot 10^{-4}\ T^2\zeta - 4.35 \cdot 10^{-7}\ T^3\zeta \end{aligned} \tag{61}$$

Obviously, this correction function is independent of the nature of the solute. Eqn. 61 allows the calculation of $\Delta\mu^{(D)}$ at any point of the experimental domain with an error of about ± 1 cal mol^{-1}. For the calculation of the corresponding thermodynamic functions, the following two methods, A and B, can be applied.

Method A. With the aid of eqn. 12 and the coefficients listed in Table VIII, chemical potentials, $\Delta\mu_j$, are calculated at every 10 K interval in the experimental temperature range, also indicated in Table VIII. At every point, $\Delta\mu_j^{(D)}$ is calculated with the aid of eqn. 61, then the thermodynamic functions $^{\infty}\Delta H_j^{(D)}$, $^{\infty}\Delta S_j^{(D)}$, $\Delta C_{P,j}^{(D)}$, $h_j^{(D)}$ and $s_j^{(D)}$ are calculated by fitting an equation, formally identical with eqn. 12, to the points by non-linear regression.

Method B. For the developement of this method, first a set of $9 \times 5 = 45$ points of the "standard chemical potential difference", $\Delta\mu - \Delta\mu^{(D)}$ (eqn. 61) was calculated at every 10 K in the temperature interval 110–190°C for the five stationary phases. On this data set, eqn. 12 was fitted where the corresponding coefficients gave the necessary corrections listed in eqns. 62–66.

$$^{\infty}\Delta H_j^{(D)} = {}^{\infty}\Delta H_j + 580.2 \pm 0.6 \qquad \text{cal mol}^{-1} \tag{62}$$

$$^{\infty}\Delta S_j^{(D)} = {}^{\infty}\Delta S_j + 7.9267 \pm 0.0015 \qquad \text{cal mol}^{-1}\ \text{K}^{-1} \tag{63}$$

$$\Delta C_{P,j}^{(D)} = \Delta C_{p,j} + 0.53 \pm 0.01 \qquad \text{cal mol}^{-1}\ \text{K}^{-1} \tag{64}$$

$$h_j^{(D)} = h_j - 29.5 \pm 0.6 \qquad \text{cal mol}^{-2}\ \text{kg} \tag{65}$$

$$s_j^{(D)} = s_j - 0.1188 \pm 0.0015 \qquad \text{cal mol}^{-2}\ \text{K}^{-1}\ \text{kg} \tag{66}$$

From eqn. 65 it is seen that if the solutions are equithermal in terms of molality, they are not on a molar basis.

In order to find the set of equations for the case "$s^{(D,0)}$" *i.e.*, "$s^{(D,0)}$ only", the enthalpic coefficient of variation is $h_j^{(D,0)} = 0$. The value of α_j^* to be used for this case is found from eqns. 58 and 65:

$$\alpha_j^* = -\frac{29.5\bar{\zeta}}{T^\dagger s_j^{(0)}} \tag{67}$$

Substitution of eqn. 67 in eqns. 56–59 and using the result in eqns. 62, 63, 65 and 66 gives (same units as in eqns. 62–66)

$$^{\infty}\Delta H_j^{(D,0)} = {}^{\infty}\Delta H_j^{(0)} + 552.3 \tag{68}$$

$$^{\infty}\Delta S_j^{(D,0)} = {}^{\infty}\Delta S_j^{(0)} + 7.8614 \tag{69}$$

$$h_j^{(D,0)} = 0 \tag{70}$$

$$s_j^{(D,0)} = s_j^{(0)} - 0.0496 \tag{71}$$

It can now be shown that eqn. 49 is also valid for $h_j^{(D,1)}$ and $s_j^{(D,0)}$ with $\varphi = \bar{\zeta}$. Therefore, eqn. 51 is also valid and a set of equations can also be given for the functions related to $K_{D,j}$ having exactly the same form as eqns. 56–59:

$$^{\infty}\Delta H_j^{(D)} = {}^{\infty}\Delta H_j^{(D,0)} + T^\dagger \alpha_j^{(D)} s_j^{(D,0)} = {}^{\infty}\Delta H_j^{(D,0)} + 403.2\alpha_j^{(D)} s_j^{(D,0)} \tag{72}$$

$$^{\infty}\Delta S_j^{(D)} = {}^{\infty}\Delta S_j^{(D,0)} + \bar{\zeta}\alpha_j^{(D)} s_j^{(D,0)} = {}^{\infty}\Delta S_j^{(D,0)} + 0.945\alpha_j^{(D)} s_j^{(D,0)} \tag{73}$$

$$h_j^{(D)} = -\alpha_j^{(D)} \cdot \frac{T^\dagger}{\bar{\zeta}} \cdot s_j^{(D,0)} = -426.7\, \alpha_j^{(D)} s_j^{(D,0)} \tag{74}$$

$$s_j^{(D)} = [1 - \alpha_j^{(D)}] s_j^{(D,0)} \tag{75}$$

In summary, for the conversion of thermodynamic data related to the molal Henry coefficient, g_j, thermodynamic quantities, $X_j^{(0)}$, given in Table VIII can be transformed to those, $X_j^{(D,0)}$, related to the distribution coefficient, K_D, with the aid of eqns. 68–71 and 64. For the coefficients $h_j^{(D)}$ and $s_j^{(D)}$, the same correlation is valid as that shown for h_j and s_j in eqn. 49 with $\varphi = \bar{\zeta}$. Therefore, standard chemical potentials, $\Delta\mu_j^{(D)}$, can also be calculated with coefficients given by eqns. 72–75 if the value of $\alpha_i^{(D)}$ does not exceed *ca.* ±2.

Solution data in the homologuous series of n-alkanes

The relationship between the partial molar solution entropy and enthalpy of the n-alkanes in a hypothetical paraffin of infinite molecular weight at $T^{\dagger}$ was calculated by using data listed in Table VIII. Linear regression gave

$$^{\infty}\Delta S_z^{(0)} = \kappa + \frac{^{\infty}\Delta H_z^{(0)}}{\Theta} = -9.402\ (\pm 0.065) + \frac{^{\infty}\Delta H_z^{(0)}}{808.7\ (\pm 4.6)} \quad \text{cal mol}^{-1}\ \text{K}^{-1} \qquad (76\text{a})$$

where κ and Θ are constants. Actually, Θ is a characteristic temperature of the paraffin stationary phase. At this temperature, the difference between the homologuous paraffins would be zero, as will be seen in the following equations. For the regression eqn. 76a, only data for n-alkanes with $z = 6$–11 were used. The error of a single value around the regression line is $\Delta_{95} = \pm 0.13$ cal mol^{-1} K^{-1}. The inverse relationship, explicit for $\Delta H_z^{(0)}$, is given by

$$^{\infty}\Delta H_z^{(0)} = 808.7\ (\pm 4.6)\ ^{\infty}\Delta S_z^{(0)} + 7602\ (\pm\ 95) \qquad \text{cal mol}^{-1} \qquad (76\text{b})$$

The molar enthalpy of the n-alkanes varies linearly with the carbon number:

$$^{\infty}\Delta H_z^{(0)} = {}^{\infty}\Delta H_0^{(0)} + {}^{\infty}\delta H_z^{(0)} z = -467.7\ (\pm\ 17.0) - 1002.6\ (\pm\ 2.0) z \quad \text{cal mol}^{-1} \qquad (77)$$

where $^{\infty}\Delta H_0^{(0)}$ is the molar solution enthalpy of a hypothetic "nullane", (hydrogen), and $^{\infty}\delta H_z^{(0)}$ is that of a methylene groupe. The error of a single value is $\Delta_{95} = \pm 20$ cal mol^{-1} around the correlation line. The coefficient of variation of the molar standard entropy with the variable ζ, $s_z^{(0)}$, also gives a linear correlation with the carbon number:

$$s_z^{(0)} = s_0^{(0)} + \delta s_z^{(0)} z = 0.2820\ (\pm\ 0.0001) + 0.0174 z \quad \text{cal mol}^{-2}\ \text{kg K}^{-1} \qquad (78)$$

with analogous interpretation of the correlation constants $s_0^{(0)}$ and $\delta s_z^{(0)}$ as before. The error of a single value is $\Delta_{95} = \pm 0.0001$ around the correlation line. Finally, the correlation of $\Delta C_{p,z}$ and z is given by

$$C_{p,z} = C_{p,0} + \delta C_{p,z} z = -2.94 + 1.78 z \qquad \text{cal mol}^{-1}\ \text{K}^{-1} \qquad (79)$$

Combination of eqns. 76a and 77 gives the relationship between $^{\infty}\Delta S_z^{(0)}$ and z:

$$\begin{aligned} ^{\infty}\Delta S_z^{(0)} &= \kappa + \frac{^{\infty}\Delta H_0^{(0)}}{\Theta} + \frac{^{\infty}\delta H_z^{(0)}}{\Theta} \cdot z = {}^{\infty}\Delta S_0^{(0)} + {}^{\infty}\delta S_z^{(0)} z \\ &= -9.981\ (\pm\ 0.082) - 1.240\ (\pm\ 0.009) z \qquad \text{cal mol}^{-1}\ \text{K}^{-1} \qquad (80) \end{aligned}$$

Substitution of eqns. 76–79 in eqn. 44 gives the increase in the standard chemical potential due to the introduction of a methylene group in an n-alkane.

$$\begin{aligned}\delta\mu_z &\equiv \Delta\mu_{z+1} - \Delta\mu_z \\ &= \underbrace{\underbrace{{}^{\infty}\delta H_z^{(0)}\left(1 - \frac{T^{\dagger}}{\Theta}\right)}_{{}^{\infty}\delta\mu_z^{(\dagger)}} - \delta s_z^{(0)} T^{\dagger}\zeta}_{\delta\mu_z^{(\dagger)}} - \frac{{}^{\infty}\delta H_z^{(0)}}{\Theta} \cdot \Delta T - \delta s_z^{(0)} \Delta T\zeta - \frac{\delta C_{p,z}}{2T^{\dagger}} \cdot \Delta T^2\end{aligned} \qquad (81)$$

where ${}^{\infty}\delta\mu_z^{(\dagger)}$ is the methylene increment on the stationary phase of infinite molecular weight at temperature $T^{\dagger}$.

On the basis of the relationships summarized in eqns. 76–81 there is a linear correlation between the molar standard enthalpy, entropy and the carbon number z at all temperatures on all stationary phases.

Thermodynamic functions and retention index

The exact relationship between the standard chemical potential and the retention index is given in eqn. 14. Substitution of eqn. 12 in eqn. 14 gives a complicated but precise relationship between the retention index as a function of the thermodynamic data and of the variables ζ and ΔT around the standard temperature $T^{\dagger} = 403.15$ K. Substitution the regression eqns. 76–81 in the resulting relationship then applying the approximation $(1 - \delta)^{-1} \approx 1 + \delta$ gives eqn. 82 after tedious calculations, rearrangements and neglecting higher order terms.

$$\begin{aligned}I_j \approx {}^{\infty}I_j^{\dagger} &- \frac{100T^{\dagger}}{{}^{\infty}\delta H_z^{(0)}} \cdot \frac{\Theta}{\Theta - T^{\dagger}} \cdot \delta s_{j/z}^{(0)}\,\zeta - \frac{100}{{}^{\infty}\delta H_z^{(0)}} \cdot \frac{\Theta}{\Theta - T^{\dagger}} \cdot {}^{\infty}\delta S_{j/z}^{(0)}\,\Delta T + \\ &- \frac{100}{{}^{\infty}\delta H_z^{(0)}}\left(\frac{\Theta}{\Theta - T^{\dagger}}\right)^2 \left[\delta s_{j/z}^{(0)} + \frac{T^{\dagger}\delta s_z^{(0)}}{{}^{\infty}\delta H_z^{(0)}} \cdot {}^{\infty}\delta S_{j/z}^{(0)}\right]\zeta\,\Delta T\end{aligned} \qquad (82)$$

where ${}^{\infty}I_j^{\dagger}$ is the retention index at 130°C ($T = T^{\dagger}$) on the stationary phase of infinite molecular weight ($\zeta = 0$). In eqn. 82

$${}^{\infty}\delta S_{j/z}^{(0)} = [{}^{\infty}\Delta S_j^{(0)} - {}^{\infty}\Delta S_z^{(0)}] - i_j^0 \cdot \frac{{}^{\infty}\delta H_z^{(0)}}{\Theta} \qquad (82a)$$

and

$$\delta s_{j/z}^{(0)} = [s_j^{(0)} - s_z^{(0)}] - i_j^{(0)}\,\delta s_z^{(0)} \qquad (82b)$$

where $i_j^0 = ({}^{\infty}I_j^{\dagger} - 100z)/100$. The physical meaning of ${}^{\infty}\delta S_{j/z}^{(0)}$ is illustrated in Fig. 7. In fact, it is the difference between the solution entropy of the solute j and that of a hypothetical *n*-alkane with carbon number $z + i_j^0 = {}^{\infty}I_j^{\dagger}/100$. The physical meaning of $\delta s_{j/z}^{(0)}$ is analogous.

Comparison of eqn. 82 with eqn. 14 gives the relationships summarized in eqns. 83a–c.

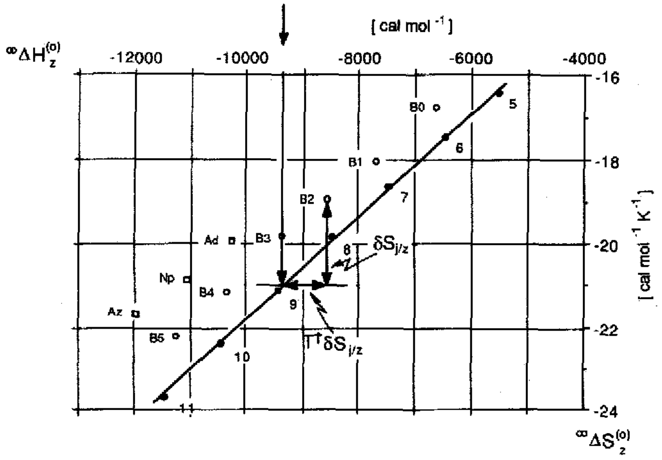

Fig. 7. Illustration of the meaning of $^{\infty}\delta S_{j/z}^{(0)}$ on the example of ethylbenzene, $^{\infty}I^{\dagger} = 891.9$. The enthalpy of an *n*-alkane with this index would be $^{\infty}\Delta H_8^{(0)} + 0.92 \cdot 1003 = -9402$ cal mol^{-1}. The solid line is the correlation between enthalpy and entropy of the *n*-alkanes. Points marked by B0–B5 are alkylbenzenes, from benzene (B0) to pentylbenzene (B5); Az is for azulene, Np for naphthalene and Ad for adamantane.

$$A_T \approx -\frac{100}{^{\infty}\delta H_z^{(0)}} \cdot \frac{\Theta}{\Theta - T^{\dagger}} \cdot {}^{\infty}\delta S_{j/z}^{(0)} = +0.199\ (\pm\ 0.001)\ {}^{\infty}\delta S_{j/z}^{(0)} \tag{83a}$$

$$A_{\zeta} \approx -\frac{100T^{\dagger}}{^{\infty}\delta H_z^{(0)}} \cdot \frac{\Theta}{\Theta - T^{\dagger}} \cdot \delta s_{j/z}^{(0)} = +80.2\ (\pm\ 0.5)\ \delta s_{j/z}^{(0)} \tag{83b}$$

$$\begin{aligned} A_{T,\zeta} &\approx -\frac{100}{^{\infty}\delta H_z^{(0)}} \left(\frac{\Theta}{\Theta - T^{\dagger}}\right)^2 \left[\delta s_{j/z}^{(0)} + \frac{T^{\dagger}\delta s_z^{(0)}}{^{\infty}\delta H_z^{(0)}}\, \delta s_{j/z}^{(0)}\right] \\ &= \frac{\Theta}{\Theta - T^{\dagger}} \left[\frac{A_{\zeta}}{T^{\dagger}} + \frac{T^{\dagger}\delta s_z^{(0)}}{^{\infty}\delta H_z^{(0)}} A_T\right] \\ &= 0.397\ (\pm\ 0.044)\ \delta s_{j/z}^{(0)} - 0.0028\ (\pm\ 0.0014)\ \delta s_{j/z}^{(0)} \\ &= 0.00495\ (\pm\ 0.00055) A_{\zeta} - 0.014\ (\pm\ 0.007) A_T \end{aligned} \tag{83c}$$

It is seen that $A_{T,\zeta}$ is a function of A_T and A_{ζ}.

The numerical value of $\delta S_{j/z}^{(0)}$ and that of $\delta s_{j/z}^{(0)}$ were calculated with eqns. 82a and b from the data listed in Table VIII. In the calculation, the index $^{\infty}I_j^{\dagger}$ listed in the second line was used, resulting from regression eqn. 13. In Figs. 8–10, the correlation between the coefficients A_T and A_{ζ} and $A_{T,\zeta}$ are shown with those calculated with the aid of eqns. 83a, b and c. The slope of the correlation lines for A_T and A_{ζ} do not deviate significantly from unity (0.93 ± 0.13 and 0.971 ± 0.028, respectively) if some results are ignored where the experimental temperature domain was too restricted. The correlation is poor but significant for $A_{T,\zeta}$ (slope 0.59 ± 0.13).

It is now clear that in turn the coefficients A_T and A_{ζ} permit the calculation of

${}^{\infty}\Delta H_j^{(0)}$, ${}^{\infty}\Delta S_j^{(0)}$ and $s_j^{(0)}$ if ${}^{\infty}\delta H_j^{(0)}$, Θ and the other thermodynamic functions of the *n*-alkanes are known. The value of i_j^0 is calculated from the definition of the index as follows:

$$i_j^0 = \frac{{}^{\infty}\Delta H_j^{(0)} - T^{\dagger}\,{}^{\infty}\Delta S_j^{(0)} - [{}^{\infty}\Delta H_z - T'\Delta S_z^{(0)}]}{{}^{\infty}\delta H_z^{(0)}\left(1 - \dfrac{T^{\dagger}}{\Theta}\right)} \tag{84}$$

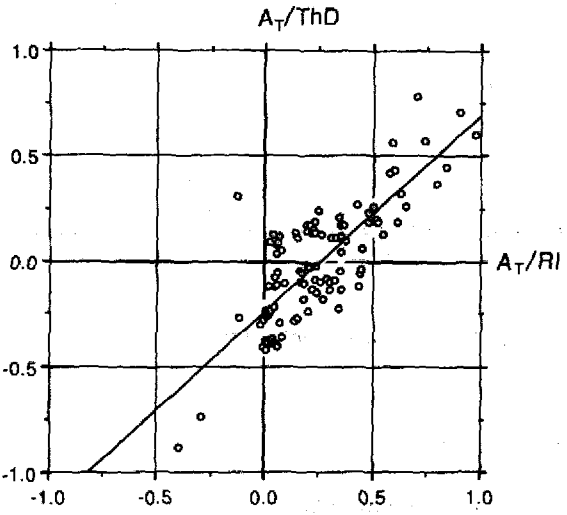

Fig. 8. Correlation of the temperature dependence of the retention index, A_T/RI, with that estimated from thermodynamic data, A_T/ThD.

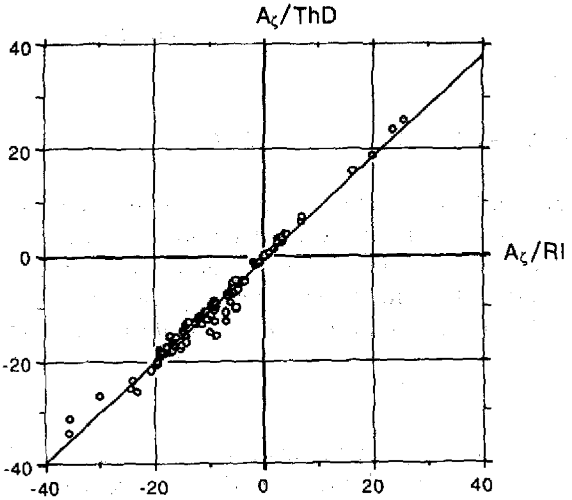

Fig. 9. Correlation of the coefficient of the dependence of the retention index on the inverse of the molecular weight, of the paraffin stationary phase, A_ζ/RI, with that estimated from thermodynamic data, A_ζ/ThD.

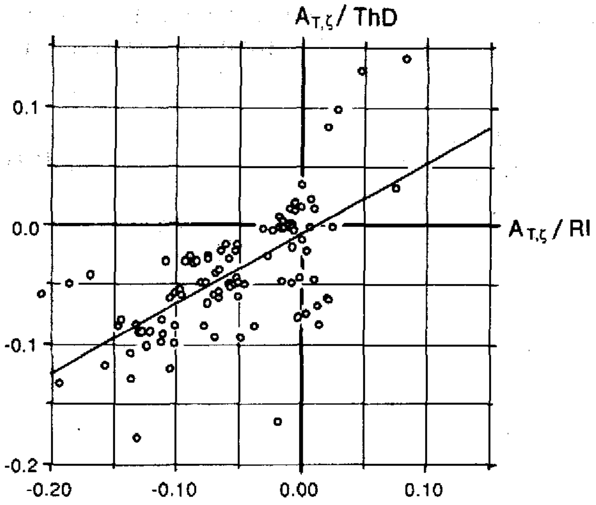

Fig. 10. Correlation of the coefficient, $A_{T,\zeta}/RI$, of eqn. 13 with that estimated from thermodynamic data, $A_{T,\zeta}/ThD$.

After some rearrangements, eqn. 84 gives for the molar enthalpy

$$\begin{aligned} {}^{\infty}\Delta H_j^{(0)} &= {}^{\infty}\Delta H_z^{(0)} + i_j^0\,{}^{\infty}\delta H_z^{(0)} + T^{\dagger}\,{}^{\infty}\delta S_{j/z}^{(0)} \\ &= {}^{\infty}\Delta H_z^{(0)} - i_j^0 \cdot 1002.6 + 2026A_T \end{aligned} \qquad (85)$$

The value of ${}^{\infty}\Delta S_j^{(0)}$ is calculated by rearranging eqn. 82a:

$${}^{\infty}\Delta S_j^{(0)} = {}^{\infty}\Delta S_z^{(0)} + i_j^0 \cdot \frac{{}^{\infty}\delta H_z^{(0)}}{\Theta} + {}^{\infty}\delta S_{j/z}^{(0)} = {}^{\infty}\Delta S_z - i_j^0 \cdot 1.240 + 5.03A_T \qquad (86)$$

Similar rearrangement of eqn. 82b gives

$$s_j^{(0)} = s_z^{(0)} + i_j^0\,\delta s_z^{(0)} + \delta s_{j/z}^{(0)} = s_z^{(0)} + i_j^0 \cdot 0.0174 + 0.0125A_\zeta \qquad (87)$$

In conclusion, the coefficients of eqn. 13 describing the variation of the retention index with temperature and with the variable ζ, permit the calculation of the molar solution enthalpy and entropy if thermodynamic data of the *n*-alkanes are known. However, the function $\Delta C_{P,j}$ cannot be estimated with data having the present error. In fact, this function should be estimated from the quadratic dependence of the index on the temperature.

General validity of the results

It has been demonstrated that the solution behaviour of a large collection of solutes can be described by eqn. 48. Comparison with literature data can be made in two steps. First, data for *n*-alkanes will be examined, then the behaviour of retention indices of other solutes.

In Fig. 11, the specific retention volume of *n*-alkanes is shown on a logarithmic scale as a function of the variable ζ at 100°C. Data were calculated with eqn. 12 and the coefficients listed in Table VIII by extrapolating down to $\zeta = 0$ and up to $\zeta = 4.0$, corresponding to a stationary phase of about $C_{16}H_{34}$. The low temperature of 100°C was chosen because several literature data sets are available at this temperature on relatively volatile paraffins, Kwantes and Rijnders[23] have determined retention data of *n*-alkanes on *n*-alkane stationary phases with $x = 16$, 24, 30 and 36 carbons. In a recent work, data for *n*-alkanes were remeasured on 19,24-dioctadecyldotetracontane, paraffin A-78 in Fig. 1[24]. Data from this reference do not deviate more than ±2% from the correlation lines. This same hydrocarbon was used in previous work as a member of a homologous series of the general formula shown in Fig. 1. In fact, retention data reported in this reference did deviate by about 15% from the present

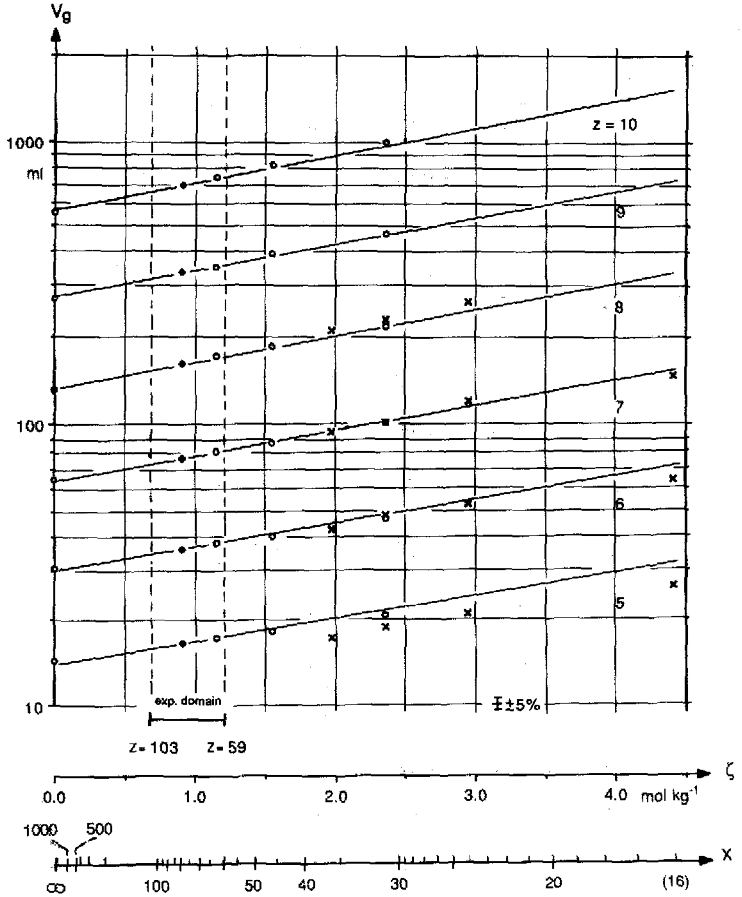

Fig. 11. Comparison of the results of this study with literature data on the example of the specific retention volumes of *n*-alkanes at 100°C (log V_g is proportional to the standard chemical potential difference). Full lines are traces of retention data calculated with eqn. 12 and coefficients listed in Table VIII. Data from (◆) Dutoit[24] (on A-78); (○) Huber[3] (on A-30, A-46, A-62); and (×) Kwantes and Rijnders[23] (on C_{16}, C_{24}, C_{32} and C_{36} *n*-alkanes).

TABLE IX

COMPARISON OF THE COEFFICIENTS OF EQN. 13, $^{\infty}I^{t}$, A_T AND A_ζ MEASURED IN THIS WORK WITH THOSE FOUND ON PARAFFIN HYDROCARBONS OF THE SERIES A-*x* WITH CARBON NUMBERS 30, 46, 62 AND 78 IN REF. 3

Under P are listed average values of $10A_T$ and A_ζ found in this work and under δ are averages of the deviations, this work − ref. 3. Compound numbers are as in Table VIII.

Compounds	$^{\infty}I^{t}$:	$10A_T$		A_ζ	
	δ	*P*	δ	*P*	δ
Hydrocarbons					
1-Alkenes					
11.05–11.11	+0.4	+ 0.32	−0.02	+1.61	−0.5
1-Alkynes					
12.05–12.10	+3.4	+ 0.52	+0.06	+4.24	−1.8
Monocyclic hydrocarbons					
13.05	+2.7	+ 3.48	+1.25	−7.0	−2.2
13.06	+4.0	+ 3.52	+0.15	−8.6	−1.4
13.07	−0.4	+ 4.83	−0.56	−11.6	+0.7
13.08	+1.9	+ 6.15	−0.69	−14.7	−0.9
Bicyclic hydrocarbons					
14.01–14.04	+4.1	+ 7.05	−0.84	−18.4	−2.6
Alkylbenzenes					
15.00–15.03	+1.5	+ 4.47	+1.08	−15.6	−1.4
Miscellaneous					
19.01	+4.3	+10.23	+0.51	−20.7	−1.9
19.03–19.04	−9.4	+ 8.37	−0.74	−41.8	+7.0
Alkane derivatives					
1-Chloroalkanes					
20.04–20.07	+3.7	+ 2.22	−0.08	−9.5	−1.6
1-Bromoalkanes					
21.02–21.07	+6.8	+ 3.08	−0.09	−10.7	+0.4
1-Iodoalkanes					
22.02–22.04	+2.2	+ 4.55	+0.70	−16.7	−3.2
1-Cyanoalkanes					
23.03–23.06	−7.9	+ 1.83	+1.64	−6.3	+4.1
23.07–23.08	+8.3	+ 2.05	+1.76	−12.1	−4.3
1-Nitroalkanes					
24.02–24.06	−2.1	+ 2.72	+0.25	−9.5	+0.5
1-Acetoxyalkanes					
25.02–25.06	+8.2	+ 0.14	+0.40	−5.3	−3.4
1-Alkanols					
31.03–31.08	+3.5	+ 2.21	+0.42	−11.2	−1.5
2-Alkanols					
32.04, 32.06–32.07	+15.5	+ 0.22	−0.72	−15.5	−9.1
2-Methyl-2-alkanols					
33.05–33.08	+9.3	+ 0.53	−1.05	−10.1	−4.2
2-Alkanones					
40.04–40.09	−1.9	+ 2.02	+0.90	−5.1	+1.5
Ethers					
41.06–41.10	+2.2	0.00	+0.38	−0.1	−1.5
Halogenomethanes					
42.22	−1.1	+ 5.29	+4.48	−8.7	+0.9
42.23	+1.8	+ 3.46	+2.23	−10.3	−5.8
43.24	+2.9	+ 2.85	+0.38	−9.1	+1.7
43.32	+7.6	+ 5.78	+0.99	−23.5	−3.8

TABLE IX *(continued)*

Compounds	$^{\infty}I^{\dagger}$:	$10A_T$		A_{ζ}	
	δ	P	δ	P	δ
Halogenobenzenes					
50.11	+3.8	+ 3.53	+0.50	−15.0	−1.9
50.21	−1.4	+ 5.48	+0.58	−19.2	+0.5
50.31	−1.1	+ 6.51	+0.42	−24.1	+0.0
50.41	+9.9	+ 7.07	−2.58	−35.2	−6.7
Pyridine					
60.01	−5.3	+ 5.07	+0.38	−24.2	−5.9
Miscellaneous					
90.01–90.02	+14.3	+ 2.37	+0.62	−18.8	−9.2

results. However, this redetermination proves that specific retention volumes published in refs. 2 and 3 are systematically too high. The correct figures are obtained on multiplying all retention volumes by 0.864 ± 0.002. These corrected data from ref. 3 are also included in the plot in Fig. 11, where specific retention volumes of *n*-alkanes were determined on a family of branched paraffins with $x = 30$, 46, 62 and 78 carbon atoms of the general formula shown in Fig. 1 as series A-*x*.

Comparison of the coefficients $^{\infty}I^{\dagger}$, A_T and A_{ζ} in this work with those in ref. 3 in Table IX shows that there is a good general correlation of the results found in both studies. It is observed that there is a close correlation between the deviation between the values of $^{\infty}I^{\dagger}$ and those found between the coefficients A_{ζ}. It is believed that this correlation is due to the fact that on stationary liquids of the series A-*x* data could not be determined at higher temperatures and thus the experimental design was unbalanced.

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