

# Solute–solvent interaction parameters by gas chromatography

Ervin sz. Kováts<sup>a,b,\*</sup>, György Fóti<sup>a</sup>, András Dallos<sup>b</sup>

<sup>a</sup> Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

<sup>b</sup> Department of Physical Chemistry, University of Veszprém, P.O. Box 158, H-8201 Veszprém, Hungary

Received 23 March 2004; received in revised form 18 June 2004; accepted 18 June 2004

Dedicated to the memory of Csaba Horváth.

## Abstract

Gas–liquid distribution coefficients at ideal dilution in non-volatile solvents can be measured by gas chromatography. The numerical value of a coefficient depends on the choice of the concentration unit in the solvent and in the gas phase. The relationships between different coefficients characterizing gas–liquid equilibria are discussed and summarized. Coefficients determined at several temperatures permit calculation of the standard chemical potential difference of the solute with the ideal gas phase as reference as a function of temperature, the *g-SPOT*. Following the proposal of Kirchhoff the latter can be formulated as an equation with three constants. As in the gas phase the molecules of the solute have no interacting partners, the three constants,  $\Delta H$ ,  $\Delta S$  and  $\Delta C$ , characterize the interaction between solvent and solute molecules. They will be called the “solute–solvent interaction parameters”. In the same system the values of these parameters depend on the choice of the distribution coefficient. Five different distribution coefficients result five sets of interaction parameters. It is shown that conversion of a parameter set to another implies additive corrections independent of the nature of the solute. If *g-SPOT*-s are measured in a series of solvents, the data may be used to calculate the corresponding liquid–liquid partition coefficients by electing one of the solvents as reference (*l-SPOT*). The corresponding “relative interaction parameters” can be calculated by simple subtraction. In a second chapter the precautions are summarized, necessary for gas chromatographic determination of distribution coefficients and examples are given for interaction parameters in different systems. It is concluded that there are significant differences between *g-SPOT*-s related to different distribution coefficients. On the other hand, differences between *l-SPOT*-s are negligible.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Solute–solvent interaction parameters; Distribution coefficients; Thermodynamic relationships

## 1. Introduction

A distribution coefficient is the ratio of the concentrations of a solute, *i*, in two phases at equilibrium. In classical thermodynamics the concentration of the solute in the gas phase, *g*, is characterized as pressure,  $P_i$ , and the concentration in a condensed phase as mole fraction,  $x_i$ . The ratio of the concentrations of a solute at ideal dilution between these two phases,  $P_i/x_i$ , is the (classical) Henry coefficient,  $h'_i$ , of the solute. Knowledge of the Henry coefficient between the ideal gas phase, *g*, and the ideal dilute solution in a solvent, *sv*, at a

given temperature permits calculation of the standard chemical potential difference,  $\Delta\mu_i^{(sv/g)}$ , the *g-SPOT*. Knowledge of the *g-SPOT* at several temperatures shows that it is a slightly curved function of temperature. Following the proposal of Kirchhoff the function,  $\Delta\mu_i^{(sv/g)}(T)$ , can be described by an equation having three constants which may be interpreted as the enthalpy of dissolution of the solute in the solvent,  $\Delta H_i^{(sv/g)}(T^\ddagger)$ , the difference of the molar entropy of the solute between the two phases,  $\Delta S_i^{(sv/g)}(T^\ddagger)$ , both at a reference temperature,  $T^\ddagger$ , and as the partial molar heat capacity difference of the solute in the two phases at constant pressure,  $\Delta C_{P,i}^{(sv/g)}$ . Latter is considered to be constant in a large enough temperature domain around a reference temperature ( $\approx T^\ddagger$

\* Corresponding author. Tel.: +41 21 6933131; fax: +41 21 3128283.

E-mail address: [ervin.kovats@epfl.ch](mailto:ervin.kovats@epfl.ch) (E. sz. Kováts).

$\pm 100^\circ\text{C}$ ). In the gas phase the solute molecules have no interaction partners, hence these constants characterize the interaction between solvent and solute molecules and they will be called the “solute–solvent interaction parameters”. Knowledge of the *g-SPOT* at more than three temperatures permits calculation of the Kirchhoff function by regression, i.e. the determination of the three interaction parameters.

In a gas chromatographic column the solute is distributed between the gas phase and the stationary phase. In the case of gas–liquid chromatography the solute is retained by absorption and adsorption. If adsorption at the liquid/gas and the liquid/support interface is negligible the specific retention volume,  $V_{g,i} = V_{N,i}/w_{sp}$  ( $\text{cm}^3 \text{g}^{-1} \equiv \text{L kg}^{-1}$ ) is identical to a distribution coefficient which is the ratio of the molarity of the solute in the gas phase and its molality in the solvent. It will be called the “molal Ostwald coefficient”. It corresponds to the net retention volume of a solute, ( $\text{cm}^3 \text{g}^{-1}$ ), measured with a column containing one gram of non-adsorbing stationary liquid. For its calculation the mass of the solvent in the column,  $w_{sp}$ , must be known.

*Note:* In the early days of gas chromatography a “reduced specific retention volume” was proposed, defined as the value of the specific retention volume multiplied by  $T/273$ , i.e. its value at  $-0.15^\circ\text{C}$ . This retention volume has no sense and should not be used.

If the density of the solvent is known then the molar concentration in the solvent can also be calculated. Hence, the concentration of the solute in the gas phase may be given as pressure and as molarity, in the solvent as molality or molarity. The four possible ratios result four distribution coefficients having different numerical values. The related *g-SPOT*-s may be used for the evaluation of interaction parameter sets which will also have different numerical values. Finally, for the calculation of the (classical) Henry coefficient the molar mass of the solvent should be available, which is practically never known.

In the last decade several papers have treated the evaluation of interaction parameters originating from gas chromatographic data by statistical methods. The aim was to detect main causes of molecular interactions, or to find best systems for the prediction of gas–liquid distribution equilibria of solutes in industrial applications, e.g. between a perfume mixture and the gas phase. The standard chemical potential difference have been calculated in neither of these publications as it should be following the proposal of classical thermodynamics as described in the introduction. Therefore, it is important to know the signification of the differences between these parameter sets and to answer the question whether one of these sets gives the right results hence is to be preferred. Our conclusion is that either of these sets may be used for such an analysis but that the data set applied for evaluation must be homogeneous, i.e. members of the set must be related to the same sort of distribution coefficient.

The present discussion is meant as a help for writing a paper on this or similar subjects. It is focussed on the con-

version of data related to different distribution coefficients and the conversion of data originally reported in calorie with atmosphere as unit for pressure to data in Joule and the pressure in bar. We do not intend to criticise works with erroneous evaluations, hence mostly we cite our own papers. The conclusions will also be illustrated with some of our published experimental results.

In the following, units will be used which are accepted by the International Union of Pure and Applied Chemistry as multiples of basic SI units [1]. Pressure is given as (bar) which is equal to  $10^5$  Pa, volume as (L) which is defined as  $1 \text{ dm}^3 (=1000 \text{ cm}^3)$ , the length as (cm) or its multiples, the mass as (kg), the molar mass as ( $\text{kg mol}^{-1}$ ), finally energy as (J) equal to  $1 \text{ kg m}^2 \text{ s}^{-2}$ . The relationship between degree centigrade and thermodynamic temperature is:  $T (\text{K}) = t (^\circ\text{C}) + 273.15$ . In this system the value of the molar gas constant is  $R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ , corresponding to ( $10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1}$ ). In order to avoid numerical factors in the equations it is preferable to define two molar gas constants: one related to energy,  $R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$  and the second to pressure,  $\Re = 0.08314472 \text{ L bar mol}^{-1} \text{ K}^{-1}$ . We have chosen this solution.

The calorie (cal) and the atmosphere (atm) are often encountered in the literature for reporting data. For the conversion of,  $\text{atm} \rightarrow \text{bar}$ , the following factor is accepted:  $1 \text{ atm} = 1.01325 \text{ bar}$ . For the conversion,  $\text{cal} \rightarrow \text{J}$ , we adopt the proposal of the National Bureau of Standards:  $1 \text{ cal} = 4.184 \text{ J}$  [2]. With this equality the molar gas constant is  $R' = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Other conversion factors proposed for the calorie do not differ more than 0.5% from the NBS definition, which is less than the error of the experimental value of distribution coefficients.

In the present discussion symbols are complex because they should reflect their slightly differing significations. This is made by subscripts and superscripts which have the following logics: *related to symbol*<sub>of</sub><sup>(in)</sup> and for the standard chemical potential difference (*SPOT*): *related to*  $\Delta\mu_{of}^{(in\ sv/in\ st)}$ , where, *sv*, is for solvent and, *st*, is for the solvent elected as standard. For gas chromatography the generally used composite symbols are accepted, such as  $V_g$  for the specific retention volume [3]. In this case the subscript is separated of the following subscript by a comma, e.g.  $V_{g,i}$ .

## 2. Characterization of distribution equilibria

### 2.1. Distribution coefficients at ideal dilution

#### 2.1.1. Concentration units

The concentration of the solute, *i*, in the ideal gas phase, (*g*), having the volume,  $V^{(g)}$  (L), may be given by its partial pressure,  $P_i$  (bar), or as its molar concentration,  $c_i^{(g)}$  ( $\text{mol L}^{-1}$ ). They are related as follows:

$$P_i V^{(g)} = n_i^{(g)} \Re T \quad (\text{L bar}) \quad (1)$$

$$c_i^{(g)} = \frac{n_i^{(g)}}{V^{(g)}} = \frac{P_i}{\Re T} \quad (\text{mol L}^{-1}) \quad (2)$$

where,  $n_i^{(g)}$  (mol), is the number of moles of the solute in the gas phase and,  $\Re = 0.08314472 \text{ L bar mol}^{-1} \text{ K}^{-1}$ .

The concentration of the solute in the solvent,  $sv$ , may be given as:

$$\text{Molality } m_i^{(sv)} = \frac{n_i^{(sv)}}{w_{sv}} \quad (\text{mol kg}^{-1}) \quad (3)$$

$$\text{Molarity } c_i^{(sv)} = \frac{n_i^{(sv)}}{V_{sv}} \quad (\text{mol L}^{-1}) \quad \text{for } n_i^{(sv)} \rightarrow 0 \quad (4)$$

$$\text{Mole fraction } x_i^{(sv)} = \frac{n_i^{(sv)}}{(n_{sv} + n_i^{(sv)})} = \frac{n_i^{(sv)}}{n_{sv}} \quad (-) \quad (5)$$

for  $n_i^{(sv)} \rightarrow 0$

where  $V_{sv}$  (L) and  $w_{sv}$  (kg) are for the volume and for the mass of the solvent, respectively. For the calculation of the volume of the solvent knowledge of its density,  $\rho_{sv}$  ( $\text{g cm}^{-3} \equiv \text{kg L}^{-1}$ ), and for the calculation of its number of moles knowledge of its molar mass,  $M_{sv}$  ( $\text{kg mol}^{-1}$ ), is necessary:

$$V_{sv} = \frac{w_{sv}}{\rho_{sv}} \quad (\text{L}) \quad (6)$$

$$n_{sv} = \frac{w_{sv}}{M_{sv}} \quad (\text{mol}) \quad (7)$$

In the case of mixed solvents the molar mass of the solvent is defined as:  $M_{sv} = \sum x_j M_j$ .

The different composition scales are related as follows:

$$\frac{m_i^{(sv)}}{c_i^{(sv)}} = \frac{V_{sv}}{w_{sv}} = \frac{1}{\rho_{sv}} \quad (\text{L kg}^{-1}) \quad (8)$$

$$\frac{m_i^{(sv)}}{x_i^{(sv)}} = \frac{n_{sv}}{w_{sv}} = \frac{1}{M_{sv}} \quad (\text{mol kg}^{-1}) \quad (9)$$

$$\frac{c_i^{(sv)}}{x_i^{(sv)}} = \frac{n_{sv}}{V_{sv}} = \frac{w_{sv}}{M_{sv} V_{sv}} = \frac{\rho_{sv}}{M_{sv}} \quad (\text{mol L}^{-1}) \quad (10)$$

### 2.1.2. Gas–liquid partition coefficients

The isothermal system to be discussed is composed of a gas phase, (g), in contact with a non-volatile solvent, (sv). At a given temperature,  $T$  (K), an infinitesimal amount of a solute,  $i$ , is introduced into the gas phase. The solute is distributed between the two phases: the ideal dilute solution and the ideal gas phase. The distribution equilibrium at a given temperature may be characterized by the following coefficients:

$$\text{Ostwald coefficient } K_{D,i}^{(sv/g)} = \frac{c_i^{(sv)}}{c_i^{(g)}} \quad (-) \quad (11)$$

$$\text{Molal Ostwald coefficient } \kappa_{D,i}^{(sv/g)} = \frac{m_i^{(sv)}}{c_i^{(g)}} \quad (\text{L kg}^{-1}) \quad (12)$$

$$\text{Molar Henry coefficient } h_i^{(sv/g)} = \frac{P_i}{c_i^{(sv)}} \quad (\text{L bar mol}^{-1}) \quad (13)$$

$$\text{Molal Henry coefficient } g_i^{(sv/g)} = \frac{P_i}{m_i^{(sv)}} \quad (\text{kg bar mol}^{-1}) \quad (14)$$

$$\text{Henry coefficient } h_i'^{(sv/g)} = \frac{P_i}{x_i^{(sv)}} \quad (\text{bar}) \quad (15)$$

where the Henry coefficient given in Eq. (15) is the “classical” Henry coefficient.

If the concentration in the gas phase is given as pressure, the coefficient is called “Henry coefficient” if it is given as molarity the coefficient is called “Ostwald coefficient”. If the concentration in the solvent is given as molarity or molality,  $c_i^{(sv)}$  or  $m_i^{(sv)}$ , the coefficient is designated as “molar” or as “molal” coefficient. Concerning the gas–liquid solute concentrations Henry and Ostwald coefficients are defined in an inverse manner. The “classical” Henry coefficient,  $h_i'^{(sv/g)}$  (bar), can only be calculated if the exact composition of the solvent is known (the corresponding Ostwald coefficient,  $x_i^{(sv)}/c_i^{(g)}$ , is never used). The relationships between the five coefficients are as follows:

$$\frac{K_{D,i}^{(sv/g)}}{\kappa_{D,i}^{(sv/g)}} = \frac{c_i^{(sv)}}{m_i^{(sv)}} = \rho_{sv} \quad (\text{kg L}^{-1}) \quad (16)$$

$$K_{D,i}^{(sv/g)} h_i^{(sv/g)} = \frac{P_i}{c_i^{(g)}} = \Re T \quad (\text{L bar mol}^{-1}) \quad (17)$$

$$K_{D,i}^{(sv/g)} g_i^{(sv/g)} = \frac{c_i^{(sv)} P_i}{m_i^{(sv)} c_i^{(g)}} = \rho_{sv} \Re T \quad (\text{kg bar mol}^{-1}) \quad (18)$$

$$K_{D,i}^{(sv/g)} h_i'^{(sv/g)} = \frac{c_i^{(sv)} P_i}{x_i^{(sv)} c_i^{(g)}} = \frac{\rho_{sv} \Re T}{M_{sv}} \quad (\text{bar}) \quad (19)$$

$$\kappa_{D,i}^{(sv/g)} h_i^{(sv/g)} = \frac{P_i m_i^{(sv)}}{c_i^{(g)} c_i^{(sv)}} = \frac{\Re T}{\rho_{sv}} \quad (\text{L}^2 \text{ bar mol}^{-1} \text{ kg}^{-1}) \quad (20)$$

$$\kappa_{D,i}^{(sv/g)} g_i^{(sv/g)} = \frac{P_i}{c_i^{(g)}} = \Re T \quad (\text{L bar mol}^{-1}) \quad (21)$$

$$\kappa_{D,i}^{(sv/g)} h_i'^{(sv/g)} = \frac{P_i m_i^{(sv)}}{c_i^{(g)} x_i^{(sv)}} = \frac{\Re T}{M_{sv}} \quad (\text{L bar kg}^{-1}) \quad (22)$$

$$\frac{h_i^{(sv/g)}}{g_i^{(sv/g)}} = \frac{m_i^{(sv)}}{c_i^{(sv)}} = \frac{1}{\rho_{sv}} \quad (\text{L kg}^{-1}) \quad (23)$$

$$\frac{h_i^{(sv/g)}}{h_i'^{(sv/g)}} = \frac{x_i^{(sv)}}{c_i^{(sv)}} = \frac{M_{sv}}{\rho_{sv}} \quad (\text{L mol}^{-1}) \quad (24)$$

$$\frac{g_i^{(sv/g)}}{h_i^{(sv/g)}} = \frac{x_i^{(sv)}}{m_i^{(sv)}} = M_{sv} \quad (\text{kg mol}^{-1}) \quad (25)$$

### 2.1.3. Liquid–liquid partition coefficients

The isothermal system is composed of a gas phase, (g), in contact with two recipients one containing a non-volatile solvent, (sv), the second containing the non-volatile solvent elected as standard, (st). At the temperature,  $T$  (K), an infinitesimal amount of a solute,  $i$ , is dissolved in the reference solvent. The solute is distributed between the three phases, forming two ideal dilute solutions and an ideal gas. The two solutions being in equilibrium with the same gas phase are obviously also in equilibrium with each other. The concentrations in the two liquid phases may be given as indicated in the case of gas–liquid equilibria as molal or molar concentration or as mole fraction (see Eqs. (3)–(5)). Based on this imaginary experiment the liquid–liquid partition coefficients may be calculated from the gas–liquid partition coefficients defined in Eqs. (11)–(15) as follows:

$$K_{D,i}^{(sv/st)} = \frac{c_i^{(sv)}}{c_i^{(st)}} = \frac{K_{D,i}^{(sv/g)}}{K_{D,i}^{(st/g)}} \left( = \frac{1}{h_i^{(sv/st)}} \right) \quad (-) \quad (26)$$

$$\kappa_{D,i}^{(sv/st)} = \frac{m_i^{(sv)}}{m_i^{(st)}} = \frac{\kappa_{D,i}^{(sv/g)}}{\kappa_{D,i}^{(st/g)}} \left( = \frac{1}{g_i^{(sv/st)}} \right) \quad (-) \quad (27)$$

$$h_i^{(sv/st)} = \frac{c_i^{(st)}}{c_i^{(sv)}} = \frac{h_i^{(sv/g)}}{h_i^{(st/g)}} \quad (-) \quad (28)$$

$$g_i^{(sv/st)} = \frac{m_i^{(st)}}{m_i^{(sv)}} = \frac{g_i^{(sv/g)}}{g_i^{(st/g)}} \quad (-) \quad (29)$$

$$h_i^{(sv/st)} = \frac{x_i^{(st)}}{x_i^{(sv)}} = \frac{h_i^{(sv/g)}}{h_i^{(st/g)}} \quad (-) \quad (30)$$

As the gas phase is missing, the number of different distribution coefficients is reduced to two in addition to the “classical” Henry coefficient, i.e. we do not admit that the concentration in the two solvents,  $sv$  and  $st$ , be given in different units. We propose to delete the two Ostwald coefficients. The relationships between the three Henry coefficients are as follows:

$$\frac{h_i^{(sv/st)}}{g_i^{(sv/st)}} = \frac{\rho_{st}}{\rho_{sv}} \quad (-) \quad (31)$$

$$\frac{h_i^{(sv/st)}}{h_i^{(sv/st)}} = \frac{\rho_{st} M_{sv}}{\rho_{sv} M_{st}} \quad (-) \quad (32)$$

$$\frac{g_i^{(sv/st)}}{h_i^{(sv/st)}} = \frac{M_{sv}}{M_{st}} \quad (-) \quad (33)$$

In the case of two completely immiscible solvents the common gas phase is not necessary because in this special case the two liquid phases can be in direct contact.

## 2.2. Partition coefficient and standard chemical potential difference (SPOT)

The aim is now to calculate a standard chemical potential difference related to the equilibration process. In order to be able to find this function we have to define a process beginning with an imaginary initial standard state. The final state is of course the two phases in equilibrium.

### 2.2.1. The equilibration process in the gas–solvent system

- (1) The system is composed of two containers,  $g$ , and  $sv$ . One of the walls of the containers is common. This common wall is permeable or impermeable to solute molecules according to the will of the experimenter.
- (2) In the initial state the common wall is impermeable, hence the two containers are independent of each other. Container,  $g$ , contains the vapor of the solute,  $i$ , having the pressure,  $\varepsilon_i P^\dagger$ , where the superscript,  $\dagger$ , designates “standard”. The number,  $\varepsilon_i$ , is chosen small enough that the solute vapor be an ideal gas. Container,  $sv$ , contains the solution of the solute in a solvent at a mole fraction,  $\varepsilon_i x_i^{(sv)\dagger}$ . The number,  $\varepsilon_i$ , is the same as that chosen for the gas phase and it is small enough to have an ideal dilute solution. The solute content of a container may also be given by any other concentration unit which is proportional to those already mentioned. Hence, in the gas phase the solute content may also be given as molar concentration,  $\varepsilon_i c_i^{(g)\dagger}$  and in the solvent phase as molal or as molar concentration,  $\varepsilon_i m_i^{(sv)\dagger}$  or  $\varepsilon_i c_i^{(sv)\dagger}$ .
- (3) The process: In order to introduce the equilibration process, the experimenter allows now that the common wall be permeable to the solute. There will be flux of the solute molecules which is considered as positive for the direction: (gas  $\equiv$ ) reference phase  $\rightarrow$  second phase.
- (4) In the final state the two phases are in equilibrium. The concentration in the gas (reference) phase is characterized by,  $P_i$  (or given as  $c_i^{(g)}$ ) and in the solvent phase the concentration will be  $x_i^{(sv)}$  (or given as  $m_i^{(sv)}$  or  $c_i^{(sv)}$ ). The chemical potential of the solute in the two phases is the same, i.e. the chemical potential difference is zero.

### 2.2.2. The standard chemical potential in the gas–solvent system, the $g$ -SPOT (gas phase as reference)

Following basic thermodynamics, the standard chemical potential difference should be calculated from the classical Henry coefficient. At equilibrium the difference of the chemical potential of the solute between the two phases is zero. The resulting  $g$ -SPOT,  $\Delta\mu_i^{(sv/g)}$ , corresponds to the driving potential of the dissolution process. The  $g$ -SPOT of the solute

at a given temperature is:

$$\begin{aligned}\Delta\mu_i^{(sv/g)} &= RT \ln \left( \frac{P_i}{x_i^{(sv)}} \right) - RT \ln \left( \frac{P^\dagger}{1} \right) \\ &= RT \ln \left( \frac{h_i^{(sv/g)}}{P^\dagger} \right) \\ &= RT \ln (h_i^{(sv/g)}/\text{bar}) \quad (\text{J mol}^{-1})\end{aligned}\quad (34)$$

One can now calculate *g*-*SPOT*-s related to any of the distribution coefficients, which will be the difference of the standard chemical potential between equilibrium and standard states. The *g*-*SPOT*-s related to the other four coefficients are as follows.

The *g*-*SPOT* related to the molal Henry coefficient is given by:

$$\begin{aligned}g\Delta\mu_i^{(sv/g)} &= RT \ln \left( \frac{P_i}{m_i^{(sv)}} \right) - RT \ln \left( \frac{P^\dagger}{m^{(sv)\dagger}} \right) \\ &= RT \ln \left( \frac{g_i^{(sv/g)} m^{(sv)\dagger}}{P^\dagger} \right) \\ &= RT \ln (g_i^{(sv/g)}/\text{bar kg mol}^{-1}) \quad (\text{J mol}^{-1})\end{aligned}\quad (35)$$

The *g*-*SPOT* related to the molar Henry coefficient is given by:

$$\begin{aligned}h\Delta\mu_i^{(sv/g)} &= RT \ln \left( \frac{P_i}{c_i^{(sv)}} \right) - RT \ln \left( \frac{P^\dagger}{c^{(sv)\dagger}} \right) \\ &= RT \ln \left( \frac{h_i^{(sv/g)} c^{(sv)\dagger}}{P^\dagger} \right) \\ &= RT \ln (h_i^{(sv/g)}/\text{bar L mol}^{-1}) \quad (\text{J mol}^{-1})\end{aligned}\quad (36)$$

The *g*-*SPOT* related to the molal Ostwald coefficient is given by:

$$\begin{aligned}-\kappa\Delta\mu_i^{(sv/g)} &= RT \ln \left( \frac{m_i^{(sv)}}{c_i^{(g)}} \right) - RT \ln \left( \frac{m^{(sv)\dagger}}{c^{(g)\dagger}} \right) \\ &= RT \ln \left( \frac{\kappa_{D,i}^{(sv/g)} c^{(g)\dagger}}{m^{(sv)\dagger}} \right) \\ &= RT \ln (\kappa_{D,i}^{(sv/g)}/\text{L kg}^{-1}) \quad (\text{J mol}^{-1})\end{aligned}\quad (37)$$

Finally, the *g*-*SPOT* related to the (molar) Ostwald coefficient is given by:

$$\begin{aligned}-K\Delta\mu_i^{(sv/g)} &= RT \ln \left( \frac{c_i^{(sv)}}{c_i^{(g)}} \right) - RT \ln \left( \frac{c^{(sv)\dagger}}{c^{(g)\dagger}} \right) \\ &= RT \ln \left( \frac{K_{D,i}^{(sv/g)} c^{(g)\dagger}}{c^{(sv)\dagger}} \right) \\ &= RT \ln K_{D,i}^{(sv/g)} \quad (\text{J mol}^{-1})\end{aligned}\quad (38)$$

The superscript preceding the symbol,  $^y\Delta$ , means: related to the distribution coefficient,  $y = g_i^{(sv/g)}$ ,  $h_i^{(sv/g)}$ ,  $\kappa_{D,i}^{(sv/g)}$  or  $K_{D,i}^{(sv/g)}$ . The superscript,  $\dagger$ , designates standard states. Obviously, the number,  $\varepsilon_i$ , multiplies all concentrations hence its ratio is unity in all equations. For the latter four coefficients the standard states in the two phases at two temperatures are shown in Fig. 1. For the Ostwald coefficients the standard concentration in the gas phase is  $c_i^{(g)\dagger} = \varepsilon_i \text{ mol L}^{-1}$ , i.e. the volume of the gas phase is independent of temperature. For the Henry coefficients the standard gas phase has  $P^\dagger = \varepsilon_i \text{ bar}$  pressure, i.e. the pressure is independent of temperature.

For the calculation of the chemical potential related to the molal coefficients only the mass of the solvent must be known. For the calculation of the molar coefficients knowledge of the density of the solvent is needed. The four gas–liquid partition coefficients are related as follows (see Eqs. (16)–(22)):

$$\frac{K_{D,i}^{(sv/st)}}{\rho_{sv}} = \kappa_{D,i}^{(sv/g)} = \frac{\Re T}{(h_i^{(sv/g)} \rho_{sv})} = \frac{\Re T}{g_i^{(sv/g)}} \quad (\text{L kg}^{-1})\quad (39)$$

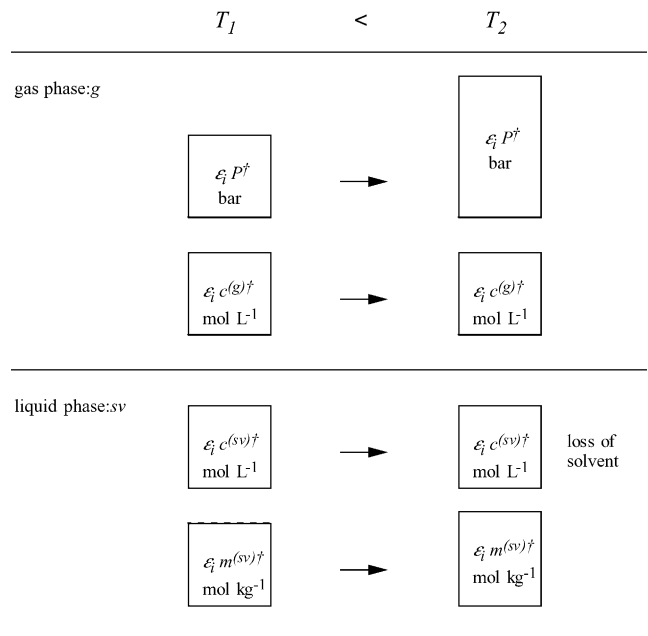


Fig. 1. The hypothetical standard states of solute,  $i$ , in the gas phase and in the liquid phase at two temperatures, where the temperature,  $T_2$ , is higher than  $T_1$ . The number,  $\varepsilon_i$  is small enough that the gas phase be ideal and that the solution of the solute in the solvent be ideal dilute. The amount of the solute must be the same at both temperatures. The surface of the frame illustrates the change of the volume at the two temperatures.

By multiplying the logarithm of Eq. (39) by  $-RT$  Eq. (40) results:

$$\begin{aligned} -RT \ln K_{D,i}^{(sv/g)} + RT \ln \rho_{sv} &= -RT \ln \kappa_{D,i}^{(sv/g)} \\ &= RT \ln h_i^{(sv/g)} - RT \ln \mathfrak{N}T + RT \ln \rho_{sv} \\ &= RT \ln g_i^{(sv/g)} - RT \ln \mathfrak{N}T \quad (\text{J mol}^{-1}) \end{aligned} \quad (40)$$

Hence, the corresponding standard chemical potential differences are related as:

$$\begin{aligned} {}^K \Delta \mu_i^{(sv/g)} + RT \ln \rho_{sv} \\ &= {}^K \Delta \mu_i^{(sv/g)} = {}^h \Delta \mu_i^{(sv/g)} - RT \ln \mathfrak{N}T + RT \ln \rho_{sv} \\ &= {}^g \Delta \mu_i^{(sv/g)} - RT \ln \mathfrak{N}T \quad (\text{J mol}^{-1}) \end{aligned} \quad (41)$$

where the symbol,  ${}^y \Delta \mu_i^{(sv/g)}$ , means: the standard chemical potential difference related to the distribution coefficient,  $y$ , of the solute,  $i$ , in the solvent,  $(sv)$ , with the ideal gas phase,  $(g)$ , as reference.

### 2.2.3. The standard chemical potential difference in a solvent–solvent system, the $l$ -SPOT (a standard solvent as reference)

For the comparison of data in different solvents it is preferred to discuss the standard chemical potential difference with reference to a solvent elected as standard. A paraffin is often chosen as a standard because such a solvent has no polar groups therefore the additional standard chemical potential in a second (polar) solvent may be attributed to the presence of polar interacting groups. The resulting  $l$ -SPOT,  $\Delta \mu_i^{(sv/st)}$ , is the driving force of the transfer of the solute from the standard solvent,  $(st)$ , into the solvent,  $(sv)$ .

For the corresponding partition coefficients see Eqs. (31)–(33). Eq. (42) gives the relationship between the two Henry coefficients of importance (see Eq. (31)):

$$h_i^{(sv/st)} = g_i^{(sv/st)} \left( \frac{\rho_{st}}{\rho_{sv}} \right) \quad (-) \quad (42)$$

Consequently:

$$RT \ln h_i^{(sv/st)} = RT \ln g_i^{(sv/st)} + RT \ln \left( \frac{\rho_{st}}{\rho_{sv}} \right) \quad (\text{J mol}^{-1}) \quad (43)$$

Hence the corresponding  $l$ -SPOT-s are related as:

$${}^h \Delta \mu_i^{(sv/st)} = {}^g \Delta \mu_i^{(sv/st)} + RT \ln \left( \frac{\rho_{st}}{\rho_{sv}} \right) \quad (\text{J mol}^{-1}) \quad (44)$$

As the gas phase is missing, the  $l$ -SPOT-s related to the Ostwald coefficients are equal to those related to the Henry coefficients.

### 2.3. Temperature dependence of the standard chemical potential difference

#### 2.3.1. Ideal gas phase as reference

Following basic thermodynamics the standard chemical potential difference of the solute,  $i$ , between the ideal gas phase and the ideal dilute solution is given by Eq. (34). Its relation to the partial molar enthalpy and entropy difference of the solute,  $\Delta H_i$  and  $\Delta S_i$ , is:

$$\begin{aligned} RT \ln h_i^{(sv/g)} &= \Delta \mu_i^{(sv/g)} \\ &= \Delta H_i^{(sv/g)} - T \Delta S_i^{(sv/g)} \quad (\text{J mol}^{-1}) \end{aligned} \quad (45)$$

where  $h_i^{(sv/g)}$ , is the “classical” Henry coefficient. Eq. (45) would suggest a linear temperature dependence of the  $g$ -SPOT, which is a good approximation in a temperature domain of about 40 °C. However, the functions,  $\Delta H$  and  $\Delta S$ , are temperature dependent. For this dependence Eqs. (46) and (47) hold.

$$\frac{\partial \Delta H_i^{(sv/g)}}{\partial T} = \Delta C_{P,i}^{(sv/g)} \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (46)$$

$$\frac{\partial \Delta S_i^{(sv/g)}}{\partial T} = \frac{\Delta C_{P,i}^{(sv/g)}}{T} \quad (\text{J mol}^{-1} \text{K}^{-2}) \quad (47)$$

where  $\Delta C_{P,i}^{(sv/g)}$ , is the partial molar heat capacity difference of the solute at constant pressure. Following the proposal of Kirchhoff we suppose that latter property is constant around a reference temperature,  $T^\dagger$ , within an appreciable temperature domain. Hence, the temperature dependence of the enthalpy and that of the entropy is given by:

$$\begin{aligned} \Delta H_i^{(sv/g)}(T) &= \Delta H_i^{(sv/g)}(T^\dagger) \\ &+ \Delta C_{P,i}^{(sv/g)}(T - T^\dagger) \quad (\text{J mol}^{-1}) \end{aligned} \quad (48)$$

$$\begin{aligned} \Delta S_i^{(sv/g)}(T) &= \Delta S_i^{(sv/g)}(T^\dagger) \\ &+ \Delta C_{P,i}^{(sv/g)} \ln(T/T^\dagger) \quad (\text{J mol}^{-1} \text{K}^{-1}) \end{aligned} \quad (49)$$

Consequently, the temperature dependence of the standard chemical potential difference is given by the Kirchhoff equation as follows:

$$\begin{aligned} \Delta \mu_i^{(sv/g)} &= \Delta H_i^{(sv/g)}(T^\dagger) - T \Delta S_i^{(sv/g)}(T^\dagger) \\ &+ \Delta C_{P,i}^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \end{aligned} \quad (50)$$

The three constants in this equation are the interaction parameters of the solute in the given solvent.

We propose now to describe the temperature dependence of the four  $g$ -SPOT-s related to the Henry and Ostwald coefficients by analogy to the Kirchhoff equation [4].

$$\begin{aligned}
{}^g\Delta\mu_i^{(sv/g)} &= {}^g\Delta H_i^{(sv/g)} - T {}^g\Delta S_i^{(sv/g)} \\
&+ {}^g\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \\
&\quad (\text{J mol}^{-1}) \quad (51)
\end{aligned}$$

$$\begin{aligned}
{}^h\Delta\mu_i^{(sv/g)} &= {}^h\Delta H_i^{(sv/g)} - T {}^h\Delta S_i^{(sv/g)} \\
&+ {}^h\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \\
&\quad (\text{J mol}^{-1}) \quad (52)
\end{aligned}$$

$$\begin{aligned}
{}^\kappa\Delta\mu_i^{(sv/g)} &= {}^\kappa\Delta H_i^{(sv/g)} - T {}^\kappa\Delta S_i^{(sv/g)} \\
&+ {}^\kappa\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \\
&\quad (\text{J mol}^{-1}) \quad (53)
\end{aligned}$$

$$\begin{aligned}
{}^K\Delta\mu_i^{(sv/g)} &= {}^K\Delta H_i^{(sv/g)} - T {}^K\Delta S_i^{(sv/g)} \\
&+ {}^K\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \\
&\quad (\text{J mol}^{-1}) \quad (54)
\end{aligned}$$

where the constants,  ${}^y\Delta H$  and  ${}^y\Delta S$ , represent the value of these functions at the reference temperature,  $T^\dagger$ .

Eqs. (51)–(54) have been written in analogy with the Kirchhoff Eq. (50), i.e. the symbols,  $\Delta H$  and  $\Delta S$  have been repeated as such, the symbol,  $\Delta C$ , has been repeated by dropping the subscript,  $P$ . In fact, in the case of the  $g$ -SPOT-s related to the Henry coefficients the use of enthalpy,  $\Delta H$  together with  $\Delta C_P$  might be justified, because for these  $g$ -SPOT-s the concentration of the solute in the gas phase is given as pressure as in the case of the  $g$ -SPOT related to the classical Henry coefficient. With this logics, for the  $g$ -SPOT-s related to the Ostwald coefficients one should substitute for these two symbols,  $\Delta U$  (the molar energy difference) and  $\Delta C_V$ , because in this case the volume of the gas phase is constant. We do not know exactly which symbols are justified, therefore we have chosen to characterize the  $g$ -SPOT-s and the three coefficients by the preceding superscript defining to which partition coefficient the function is related. This is justified because the numerical value of the four different  $g$ -SPOT-s are different. Consequently, the numerical value of the interaction parameters,  $\Delta H$ ,  $\Delta S$  and  $\Delta C$ , in the four equations are also different. In conclusion, the preceding superscript defines the standard states of the solute in both the gas and in the solvent phase.

Either of these equations describe the slightly curved  $g$ -SPOT in a temperature range of  $\approx T^\dagger$  (K)  $\pm$  100 K. The  $g$ -SPOT as a function of temperature is illustrated in Fig. 2 on the example of  ${}^g\Delta\mu_i^{(sv/g)}$  of  $n$ -octane in a paraffin solvent. For data originating from gas chromatographic measurements the choice of  $T^\dagger = (130 + 273.15)$  K is usual and adequate.

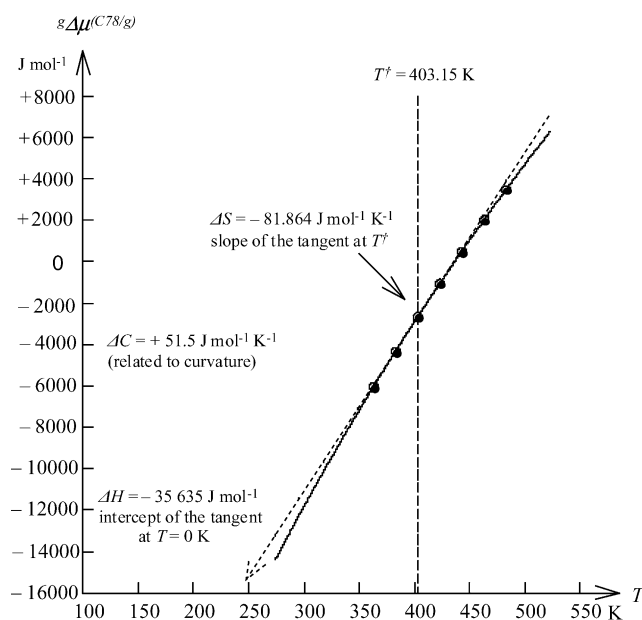


Fig. 2. A typical example of the temperature dependence of the  $g$ -SPOT related to the molal Henry coefficient:  $n$ -octane in the branched paraffin  $C_{78}$  around the standard temperature of  $T^\dagger = 130 + 273.15$  K. Partition data were determined in the temperature range of 90–210 °C with an error smaller than the diameter of a dot in the diagram. Note that  $\Delta H$  and  $\Delta S$  are negative and  $\Delta C$  is positive.

The three constants of Eqs. (51)–(54) can be calculated by regression if  $g$ -SPOT-s have been determined at at least four temperatures. Three degrees of freedom are necessary for the determination of the three constants leaving one degree of freedom for the dispersion around regression. Experimental practice has shown that it is preferable to determine  $g$ -SPOT-s at five equidistant temperature steps of 15–20 °C, i.e. in an experimental temperature range of 60–80 °C.

### 2.3.2. Ideal dilute solution in a standard solvent as reference

If the  $g$ -SPOT of a solute in both the standard solvent, ( $st$ ), and the solvent, ( $sv$ ), is known, the  $l$ -SPOT of a solute is calculated by simple subtraction. For the  $l$ -SPOT related to the molal Henry coefficient Eq. (55) holds:

$$\begin{aligned}
{}^g\Delta\mu_i^{(sv/st)} &= {}^g\Delta\mu_i^{(sv/g)} - {}^g\Delta\mu_i^{(st/g)} (\equiv -{}^\kappa\Delta\mu_i^{(sv/st)}) \\
&= {}^\kappa\Delta\mu_i^{(st/g)} - {}^\kappa\Delta\mu_i^{(sv/g)} \\
&= {}^g\Delta H_i^{(sv/st)} - T {}^g\Delta S_i^{(sv/st)} + {}^g\Delta C_i^{(sv/st)} \\
&\quad \times \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \quad (55)
\end{aligned}$$

The  $l$ -SPOT related to the molal Henry coefficient is given by Eq. (56):

$$\begin{aligned}
{}^h\Delta\mu_i^{(sv/st)} &= {}^h\Delta\mu_i^{(sv/g)} - {}^h\Delta\mu_i^{(st/g)} (\equiv -{}^K\Delta\mu_i^{(sv/st)}) \\
&= {}^K\Delta\mu_i^{(st/g)} - {}^K\Delta\mu_i^{(sv/g)}
\end{aligned}$$

$$= {}^h \Delta H_i^{(sv/st)} - T {}^h \Delta S_i^{(sv/st)} + {}^h \Delta C_i^{(sv/st)} \\ \times \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \quad (56)$$

#### 2.4. Interconversion of standard chemical potential differences

There are two principal ways to interconvert different *g-SPOT*-s. The first possibility is to use original individual data, convert them to the desired *g-SPOT*-s by using Eqs. (39)–(41) and calculate the corresponding *g-SPOT*/temperature functions by regression. In general we do not dispose of the individual data. Hence, the more important question is the relationship between the coefficients of the *g-SPOT*/temperature functions related to different distribution coefficients.

##### 2.4.1. Conversion of *g-SPOT*-s given in (cal mol<sup>-1</sup>) and (atm) → (J mol<sup>-1</sup>) and (bar)

Are known: the coefficients of a *g-SPOT*/temperature function,  ${}^g \Delta^* \mu_i^{(sv/g)}$ , or,  ${}^h \Delta^* \mu_i^{(sv/g)}$  given in units of (cal mol<sup>-1</sup>), related to either of the Henry coefficients,  $g_i^{*(sv/g)}$  or  $h_i^{*(sv/g)}$ , with the pressure of the gas phase in units of (atm). Multiplying the function by the factor 4.184, results in a *g-SPOT* in units of (J mol<sup>-1</sup>), but where the standard state of the solute, *i*, in the gas phase is in units of (atm). The two Henry coefficients are related as follows:

$$g_i^{(sv/g)} = \frac{P_i \text{ (bar)}}{m_i^{(sv)}} = \frac{1.01325 P_i \text{ (atm)}}{m_i^{(sv)}} \\ = 1.01325 g_i^{*(sv/g)} \quad (\text{kg bar mol}^{-1}) \quad (57a)$$

$$h_i^{(sv/g)} = \frac{P_i \text{ (bar)}}{c_i^{(sv)}} = \frac{1.01325 P_i \text{ (atm)}}{c_i^{(sv)}} \\ = 1.01325 h_i^{*(sv/g)} \quad (\text{L bar mol}^{-1}) \quad (57b)$$

Hence

$$RT \ln g_i^{(sv/g)} = {}^g \Delta \mu_i^{(sv/g)} = RT \ln g_i^{*(sv/g)} + RT \ln 1.01325 \\ = 4.184 {}^g \Delta^* \mu_i^{(sv/g)} + 0.10947 T \quad (\text{J mol}^{-1}) \quad (58a)$$

$$RT \ln h_i^{(sv/g)} = {}^h \Delta \mu_i^{(sv/g)} = 4.184 {}^h \Delta^* \mu_i^{(sv/g)} \\ + 0.10947 T \quad (\text{J mol}^{-1}) \quad (58b)$$

From Eqs. (58a) and (58b) follows that the interaction parameters related to the molal Henry coefficient given in calorie are related to the interaction parameters as defined in Eqs. (51) and (52) are as follows:

$${}^y \Delta H_i^{(sv/g)} = 4.184 {}^y \Delta^* H_i^{(sv/g)} \quad (\text{J mol}^{-1}) \quad (59a)$$

$${}^y \Delta S_i^{(sv/g)} = 4.184 {}^y \Delta^* S_i^{(sv/g)} - 0.10947 \quad (\text{J mol}^{-1} \text{ K}^{-1}) \\ (59b)$$

$${}^y \Delta C_i^{(sv/g)} = 4.184 {}^y \Delta^* C_i^{(sv/g)} \quad (\text{J mol}^{-1} \text{ K}^{-1}) \quad (59c)$$

where the superscript, *y*, is either *g* or *h*. For the conversion of the coefficients of *g-SPOT*-s related to Ostwald coefficients given in (cal mol<sup>-1</sup>) the interaction parameters must simply be multiplied by the factor of 4.184.

##### 2.4.2. Conversion of molal → molar *g-SPOT*-s

Conversion of a *g-SPOT* related to a molal to that related to a molar distribution coefficient is equivalent to change the standard state in the solvent from molar to molal concentration. For *g-SPOT*-s related to both the molal Henry and Ostwald coefficients Eqs. (60a) and (60b) hold:

$${}^h \Delta \mu_i^{(sv/g)} = {}^g \Delta \mu_i^{(sv/g)} - RT \ln (\rho_{sv}/\text{kg L}^{-1}) \quad (\text{J mol}^{-1}) \\ (60a)$$

$${}^K \Delta \mu_i^{(sv/g)} = {}^\kappa \Delta \mu_i^{(sv/g)} - RT \ln (\rho_{sv}/\text{kg L}^{-1}) \quad (\text{J mol}^{-1}) \\ (60b)$$

where the correcting term is:

$$\delta \mu_{\text{corr},sv} = -RT \ln (\rho_{sv}/\text{kg L}^{-1}) \quad (\text{J mol}^{-1}) \quad (61)$$

For the conversion the following procedure is suggested. First, the density of the solvent is determined at several temperatures, in the case of gas chromatography from about +30 to +250 °C. Eq. (62) is then fitted to the experimental points by regression:

$$\ln (\rho_{sv}/\text{kg L}^{-1}) = \ln \rho_{sv}^\dagger - \alpha_{sv}(T - T^\dagger) - \beta_{sv}(T - T^\dagger)^2 \\ (62)$$

where  $\rho_{sv}^\dagger$  is the density of the solvent at a standard temperature,  $T^\dagger$ , and,  $\alpha_{sv}$  and  $\beta_{sv}$ , are constants. Knowledge of the density as function of temperature permits to calculate the correcting *g-SPOT*-s with Eqs. (61) and (62) e.g. at 5 °C intervals in the whole experimental temperature domain. Eq. (63) is fitted on these points by regression:

$$\delta \mu_{\text{corr},sv} = -RT \ln (\rho_{sv}/\text{kg L}^{-1}) = \delta H_{\text{corr},sv} - T \delta S_{\text{corr},sv} \\ + \delta C_{\text{corr},sv} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \\ (63)$$

Eq. (63) is a curious description of the temperature dependence of the density of the solvent on temperature, but the fit is excellent. The correction depends only on the nature of the solvent, in a given solvent it is the same for all solutes.

$${}^h \text{ or } {}^\kappa \Delta H_i^{(sv/g)} = {}^g \text{ or } {}^\kappa \Delta H_i^{(sv/g)} + \delta H_{\text{corr},sv} \quad (\text{J mol}^{-1}) \\ (64a)$$

$${}^h \text{ or } {}^\kappa \Delta S_i^{(sv/g)} = {}^g \text{ or } {}^\kappa \Delta S_i^{(sv/g)} + \delta S_{\text{corr},sv} \quad (\text{J mol}^{-1} \text{ K}^{-1}) \\ (64b)$$



$$h \text{ or } K \Delta C_i^{(sv/g)} = g \text{ or } \kappa \Delta C_i^{(sv/g)} + \delta C_{\text{corr},sv} \quad (\text{J mol}^{-1} \text{ K}^{-1}) \quad (64c)$$

#### 2.4.3. Conversion of Henry $\rightarrow$ Ostwald $g$ -SPOT- $s$

The conversion of a  $g$ -SPOT related to molar Henry or molar Ostwald coefficient to that related to the corresponding molal coefficient is given by (see Eq. (41)):

$$\kappa \Delta \mu_i^{(sv/g)} = g \Delta \mu_i^{(sv/g)} - RT \ln \mathfrak{N}T \quad (\text{J mol}^{-1}) \quad (65a)$$

$$K \Delta \mu_i^{(sv/g)} = h \Delta \mu_i^{(sv/g)} - RT \ln \mathfrak{N}T \quad (\text{J mol}^{-1}) \quad (65b)$$

where the correcting function is:

$$\begin{aligned} \delta \mu_{\text{corr}} &= -RT \ln \mathfrak{N}T = -RT \ln \mathfrak{N} - RT \ln T \equiv RT^\dagger \\ &\quad -T[R \ln \mathfrak{N} + R \ln T^\dagger + R] \\ &\quad + R \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \quad (66) \end{aligned}$$

Compared with the correcting equation:

$$\delta \mu_{\text{corr}} = \delta H_{\text{corr}} - T \delta S_{\text{corr}} + \delta C_{\text{corr}} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \quad (67)$$

The corrections for  $T^\dagger = 403.15 \text{ K}$  can be identified as follows:

$$\begin{aligned} K \text{ or } \kappa \Delta H_i^{(sv/g)} &= h \text{ or } g \Delta H_i^{(sv/g)} + RT^\dagger = h \text{ or } g \Delta H_i^{(sv/g)} \\ &\quad + 3351.8 \quad (\text{J mol}^{-1}) \quad (68a) \end{aligned}$$

$$\begin{aligned} K \text{ or } \kappa \Delta S_i^{(sv/g)} &= h \text{ or } g \Delta S_i^{(sv/g)} + R \ln \mathfrak{N} + R \ln T^\dagger + R \\ &= h \text{ or } g \Delta S_i^{(sv/g)} + 37.5139 \quad (\text{J mol}^{-1} \text{ K}^{-1}) \quad (68b) \end{aligned}$$

$$\begin{aligned} K \text{ or } \kappa \Delta C_i^{(sv/g)} &= h \text{ or } g \Delta C_i^{(sv/g)} + R = h \text{ or } g \Delta C_i^{(sv/g)} \\ &\quad + 8.31 \quad (\text{J mol}^{-1} \text{ K}^{-1}) \quad (68c) \end{aligned}$$

#### 2.4.4. Ideal dilute solution in a standard solvent as reference

With the aid of the relationships given under Section 2.4.1, the corresponding relationships are easily found. It will be seen, that the values of the corrections to add for the conversion of the constants related to the molal Henry  $\rightarrow$  molar Henry ( $\equiv$  molal Ostwald  $\rightarrow$  molar Ostwald) are very small.

### 3. Measurement of distribution coefficients by gas–liquid chromatography

In gas chromatography retention volumes and that of the stationary phase are given in units of ( $\text{cm}^3$ ) in contrast to the foregoing discussion on distribution coefficients where

volumes are in units of (L). The mass of the stationary phase,  $sp$ , is given in (g).

#### 3.1. The ideal gas chromatographic column

The ideal column for gas/liquid chromatography is a tube containing an ideal gas and a known amount of a non-volatile solvent,  $w_{sp}$  (g), called the stationary phase,  $sp$ . The column has no flow resistance, hence it is at uniform pressure,  $P_c$ . At the column inlet an ideal gas, the carrier is introduced continuously, and its volume is measured with a gas volume meter. At the column inlet is situated an injector, at the end of the column a detector is mounted which signals the presence of a solute vapor in the carrier. The column, the injector and the detector are at constant temperature,  $T_c$  (K), injector and detector have zero volume. At the beginning of the experiment an infinitesimal volume of the vapor of a solute is introduced into the gas stream by means of the injector. The solute impulsion is distributed between the two phases but is not adsorbed at the gas–solvent interface. The part in the gas phase is transported by the carrier, where partition is instantaneous. The volume of the carrier necessary to transfer the solute to the detector is measured. This volume is called the retention volume of the solute,  $i$ , and is designated by,  $V_{R,i}$  ( $\text{cm}^3$ ). A solute insoluble in the stationary phase traverses the column with the same velocity as the carrier. Its retention volume is called the holdup volume of the column,  $V_\mu$  ( $\text{cm}^3$ ), which in the case of the ideal column is equal to the volume of the gas phase in the column.

*Note:* The expression “carrier” suggests that this gas has the only role to transport, to carry the solute molecules, but otherwise the molecules of the carrier have no interactions with the molecules of the solute.

In a gas chromatographic system where retention is made by absorption only (i.e. no adsorption at interfaces) the retention volume,  $V_{R,i}$  ( $\text{cm}^3$ ), is related to the Ostwald coefficient as follows:

$$V_{R,i} = V_\mu + V_{sp} K_{D,i}^{(sv/g)} \quad (\text{cm}^3) \quad (69)$$

where  $V_{sp}$  ( $\text{cm}^3$ ), is the volume of the stationary phase, i.e. of the non-volatile solvent in the column. The “holdup volume” of the column,  $V_\mu$  ( $\text{cm}^3$ ), is measured by injection of a gas insoluble in the stationary phase. The net retention volume is then defined as [5]:

$$V_{N,i} = V_{R,i} - V_\mu = V_{sp} K_{D,i}^{(sv/g)} \quad (\text{cm}^3) \quad (70)$$

The specific retention volume is defined as:

$$V_{g,i} = \frac{V_{N,i}}{w_{sp}} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (71)$$

where  $w_{sp}$  (g), is the amount of the stationary liquid (solvent) in the column (the subscript,  $g$ , in the symbol,  $V_{g,i}$ , means “per gram” and has nothing to do with the gas phase). For the calculation of the specific retention volume only the exact mass of the stationary liquid (the solvent) is necessary, but

its density may be unknown. Combination of Eqs. (70) and (71) gives:

$$V_{g,i} = \frac{K_{D,i}^{(sv/g)}}{\rho_{sp}} = \kappa_{D,i}^{(sv/g)} \quad (\text{cm}^3 \text{ g}^{-1}) \equiv (\text{L kg}^{-1}) \quad (72)$$

### 3.2. The real gas chromatographic column

In a real system: (a) the column has a flow resistance and (b) not the volume but the volumetric flow rate of the carrier is measured which must be constant during the experiment. For the calculation of the mean column pressure the column must be uniform. Further, the stationary phase, *sp*, must be applied on a support as a thin film, hence its specific surface area may be considerable. Consequently, retention is made not only by absorption but also by adsorption at the gas/*sp* and at the support/*sp* interfaces.

The gas chromatographic system is composed of a gas reservoir, the injector, (inj), the column, (c), the detector and the flowmeter, (fl). The following scheme shows the designation of the experimental parameters at different points of the system:

	Injector	Column		Flowmeter
Pressure	$P_{\text{inj}}^{(i)}$	$P_c^{(i)}$ $P_c^{(m)}$ $P_c^{(o)}$	=	$P_{\text{fl}} = P_{\text{atm}}$
Temperature	$T_{\text{inj}}$	$T_c$ $T_c$ $T_c$		$T_{\text{fl}} = T_{\text{room}}$
Flowrate	$\Phi_{\text{inj}}^{(i)}$	$\Phi_c^{(i)}$ $\Phi_c^{(m)}$ $\Phi_c^{(o)}$		$\Phi_{\text{fl}}$

Here superscript (i) is for inlet, (m) is for mean and, (o) is for outlet. At the injector inlet the pressure of the carrier,  $P_{\text{inj}}^{(i)}$ , is measured by determining the pressure difference between the pressure of the carrier at the system inlet and the barometric pressure (in general with a mercury manometer):  $\Delta P_{\text{inj}}^{(i)} = P_{\text{inj}}^{(i)} - P_{\text{atm}}$ . The carrier is introduced into the injector through a capillary which has a certain flow resistance. The sudden evaporation of the liquid sample introduced into the injector will generate a short volume shock. The capillary prevents a return of solvent vapors back to the cold parts of the system inlet. The temperature of the injector system,  $T_{\text{inj}}$ , is not uniform. The part where the sample is evaporated should be at column temperature,  $T_c$ , the beginning of the capillary is practically at room temperature. Therefore, the flow resistance of the injector system must be determined experimentally in the whole envisaged temperature range as follows. By omitting the column the injector outlet is connected by a large bore capillary (negligible flow resistance) to the flowmeter. Now the oven temperature is regulated at different values and the flow resistance of the injector,  $r_{\text{inj}}$ , is measured by admitting that:

$$\Delta P_{\text{inj}}^{(i)} = P_{\text{inj}}^{(i)} - P_{\text{atm}} = r_{\text{inj}} \Phi_{\text{inj}}^{(i)} = r_{\text{inj}} \Phi_{\text{fl}} \left( \frac{P_{\text{fl}}}{P_{\text{inj}}^{(i)}} \right) \quad (\text{bar}) \quad (73)$$

The viscosity of an ideal gas depends on temperature but is independent of pressure. Therefore, it is supposed that with the aid of the experimentally determined temperature dependent flow resistance of the injector system,  $r_{\text{inj}}$ , the inlet pressure drop can also be calculated at higher pressures, i.e. if the column is mounted:

$$\Delta P_{\text{corr}} = r_{\text{inj}} \Phi_{\text{inj}}^{(i)} \quad (\text{bar}) \quad (74)$$

$$P_c^{(i)} = P_{\text{inj}}^{(i)} - \Delta P_{\text{corr}} \quad (\text{bar}) \quad (75)$$

Hence, knowledge of the flow resistance, permits determination of the small pressure drop in the injector necessary for the calculation of the pressure of the carrier at the column inlet. This correction is only an approximation for small pressure drops.

- (1) It is now suggested to repeat these experiments with a void column mounted in the system. Probably, there will be no difference between the results with or without the void column. If the void column (a glass frit at the end) or the detector connections have a flow resistance, these experiments will prove it and one can introduce a correction for the pressure drop at the column end in a similar manner as that at the column inlet. In most cases this correction is negligible.
- (2) It is important to note that in commercial gas chromatographs inlet capillaries have an exaggerated flow resistance. It is recommended to change the capillary.

From the injector the carrier enters the packed column. The column filling is supposed to be uniform, hence it will have the same flow resistance per unit length at any point. The column is placed in an oven hopefully having the same temperature at any point. It is necessary to measure the temperature of the oven for example with a calibrated platinum resistance thermometer. It is recommended to measure also the temperature difference between the site of the platinum thermometer and seven points in the oven situated together with the main thermometer at the eight corners of a cube enclosing the site of the column. This can be made with the aid of thermocouples where the reference point of the thermocouples is the point where the platinum thermometer is situated. The average temperature of the eight sensors will be accepted as column temperature,  $T_c$ .

From the packed column the carrier enters the detector having the same temperature as the column then it enters the flowmeter at room temperature,  $T_{\text{fl}} = T_{\text{room}}$ . Measurement of the flow rate of the carrier is made in general with a digital or a soap film flowmeter with optical sensors. Its temperature may be controlled with a calibrated thermometer. Using a soap film flowmeter the degree of saturation of the carrier by water vapor is badly defined if the outlet of the column is directly connected to the flowmeter, because the dry carrier is only in short contact with the aqueous soap solution. Hence, it is preferred to saturate the carrier with water by passing it first through a column filled with wet cotton, then correct the

flowrate for the small water vapor content, to get the flowrate of the dry carrier,  $\Phi_{\text{fl}}$ , at  $T_{\text{fl}} = T_{\text{room}}$ , and at the pressure of the flowmeter which is equal to the atmospheric pressure,  $P_{\text{fl}} = P_{\text{atm}}$ . The main advantage of the bubble meter to be independent of the nature of the gas. In contrast, electronic flowmeters must be calibrated for a given gas or gas mixture and have an accuracy of only 2–3%. The atmospheric pressure must be measured with a barometer by applying the necessary corrections (e.g. in the case of a mercury barometer the temperature of the mercury, correction for the curvature of the mercury surface in the tube). The pressure must be controlled at least three times during a working day, especially if the weather changes seriously (stormy weather).

Are now known: the corrected pressure of the carrier at the column inlet,  $P_c^{(i)}$ , and at the column outlet,  $P_c^{(o)}$ , the temperature of the column,  $T_c$ , and that of the flowmeter,  $T_{\text{fl}} = T_{\text{room}}$ . The mean column pressure,  $P_c^{(m)}$ , can now be calculated with the equation given by Martin and James [6]:

$$P_c^{(m)} = P_c^{(o)} \left( \frac{2(\varphi^3 - 1)}{3(\varphi^2 - 1)} \right) \quad (\text{bar}) \quad (76)$$

where  $\varphi = P_c^{(i)}/P_c^{(o)}$ , is the relative pressure drop in the column. With the aid of the mean column pressure the mean flowrate can be calculated:

$$\Phi_c^{(m)} = \Phi_{\text{fl}} \left( \frac{P_{\text{fl}} T_c}{P_c^{(m)} T_{\text{fl}}} \right) \quad (\text{cm}^3 \text{ min}^{-1}) \quad (77)$$

The system is now ready for experimentation. The two necessary experimental parameters are known: the temperature of the column,  $T_c$ , and the mean flowrate of the carrier in the column,  $\Phi_c^{(m)}$ , which is an ideal gas.

### 3.3. The retention volume

#### 3.3.1. The net retention volume

The determination of the retention time,  $t_{R,i}$ , does not present a problem. We propose to inject small amounts of a solute,  $i$ , and to accept the time between injection and the appearance of the maximum of the peak as retention time,  $t_{R,i}$ . Use of helium as carrier is the best possible choice, since considering helium as an ideal gas does not introduce an appreciable error. For the determination of the starting point of the chromatogram a solute is necessary which must be also insoluble in the stationary phase. The best choice for a marker is neon, also a nearly ideal gas practically insoluble in organic solvents. The time elapsed between the appearance of the neon peak and of the solute peak is the net retention time,  $t_{N,i}$ , of the solute:

$$t_{N,i} = t_{R,i} - t_{R,\text{Ne}} \quad (\text{min}) \quad (78)$$

The net retention volume at the column temperature,  $T_c$ , is then given by:

$$V_{N,i} = t_{N,i} \Phi_c^{(m)} \quad (\text{cm}^3) \quad (79)$$

In the real system the retention volume of neon,  $V_{R,\text{Ne}} = t_{R,\text{Ne}} \Phi_c^{(m)} = V_{\mu}'$ , is not equal to the volume of the gas phase in the column,  $V_{\mu}$ , but includes undefined contributions from the volume of the injector and of the detector. The “retention factor”,  $k_i = t_{N,i}/t_{R,\text{Ne}}$ , is the net retention volume given in units of  $V_{\mu}'$ .

#### 3.3.2. The specific retention volume

For the calculation of the specific retention volume knowledge of the mass of the stationary liquid in the column is necessary. In addition, one has to prove that the effect of interfaces is negligible, i.e. that the effect of adsorption on retention is small enough to be neglected.

The loading of the support by the stationary liquid is best determined during preparation. The necessary amount of stationary liquid is weighed and dissolved in a solvent (pentane or diethyl ether). The weighed amount of a support of known specific surface area is placed in a round bottom flask and the solution is added portionwise. After addition the solution should completely cover the support. On a rotating evaporator the solvent is slowly eliminated in a gas stream and the column filling is isolated. The flask is washed with ether, the solvent is evaporated and the residue weighed to give the non-supported part of the stationary phase. The percentage SP on the support is calculated by correcting for this residue.

The void column is now weighed, packed with the prepared column filling and weighed again. Knowledge of the weight of the packing and that of the weight percentage of the SP on the column packing permit to calculate the mass of the stationary phase in the column,  $w_{sp}$ .

Adsorption is proportional to the specific surface area of the liquid which is obviously smaller on supports having a small specific surface area. The surface energy of the support must be high enough in order to complete wetting by the stationary liquid. As a first approximation, neglecting special interactions, the surface tension of the support should be somewhat higher than that of the liquid. In this case the support is wettable and the resulting interfacial tension is a minimum. In conclusion, one has to choose a support of low specific surface area and deactivate the surface without lowering the surface tension of the solid as much as to become non-wettable. The specific surface area of the liquid diminishes with higher loadings. Higher loading implies longer retention times. In order to arrive at a compromise, we propose to apply supports having specific surface areas of about  $0.5 \text{ m}^2 \text{ g}^{-1}$ , and to use of about 7% (w/w) of stationary phase. With this quantity the specific surface area of the stationary phase,  $sp$ , is about  $0.5/0.07 \approx 7 \text{ m}^2 \text{ g}^{-1}$ . This permits to calculate the surface area of the two interfaces:  $sp/\text{support}$  and  $sp/\text{gas}$ . Unfortunately one cannot influence adsorption at the  $sp/\text{gas}$  interface where negative adsorption of solutes may be important with liquids of very low surface tension.

The experimental method for choosing the lowest possible loading is the following: prepare three columns with different  $sp$ -loadings, e.g. 4, 6 and 8%. Determine specific retentions of a group of solutes at low temperatures. Plot the resulting

retention volumes as a function of the specific surface area of the *sp* in the column. Choose the loading where the effect of the adsorption is negligible. After eventual control experiments, the specific retention volume can be calculated using Eq. (71).

*Note:* The most satisfactory solution implies the determination of both contributions to retention. For this purpose retention data must be determined on at least three columns with different loadings. The results are then plotted as a function of the specific surface area of the stationary phase and extrapolated to a hypothetical stationary phase of zero specific surface area. For details see refs. [7,8].

### 3.4. Relative retention and standard chemical potential

The relative retention of solute, *i*, at temperature, *T*, is defined as:

$$r_{i/\text{ref}}^{(sv)} = \frac{V_{N,i}^{(sv)}}{V_{N,\text{ref}}^{(sv)}} = \frac{t_{N,i}^{(sv)}}{t_{N,\text{ref}}^{(sv)}} \quad (80)$$

where the retention of the solute, *i*, and that of the reference compound, ref, have been determined under the same conditions. In this case the net retention volume,  $V_N$ , or the net retention time,  $t_N$ , may also be substituted by the specific retention volume,  $V_g$ , or by any of the distribution coefficients. With the aid of the foregoing equations it is easy to show that:

$$\begin{aligned} -RT \ln r_{i/\text{ref}}^{(sv)} &= -RT \ln (V_{N,i}^{(sv)} / V_{N,\text{ref}}^{(sv)}) \\ &= -RT \ln V_{N,i}^{(sv)} + RT \ln V_{N,\text{ref}}^{(sv)} \\ &= \Delta\mu_i^{(sv/g)} - \Delta\mu_{\text{ref}}^{(sv/g)} \quad (\text{J mol}^{-1}) \end{aligned} \quad (81)$$

where the *g-SPOT* may be related to any of the distribution coefficients,  $K_D, \dots, h'$ . In conclusion, if the *g-SPOT* of the reference compound is known, the corresponding *g-SPOT* of the solute, *i*, can be calculated with Eq. (81). The use of a unique reference compound is not possible, because for the temperature dependence of the retention of solutes the following rule is valid: the net retention volume is halved when raising the temperature by 20–30 °C.

The retention index is defined as:

$$\begin{aligned} I_i^{(sv)} &= 100 \left[ \frac{\ln V_{N,i}^{(sv)} - \ln V_{N,z}^{(sv)}}{\ln V_{N,(z+1)}^{(sv)} - \ln V_{N,z}^{(sv)}} \right] + 100z \\ &= 100 \left[ \frac{\ln(V_{N,i}^{(sv)} / V_{N,z}^{(sv)})}{\ln(V_{N,(z+1)}^{(sv)} / V_{N,z}^{(sv)})} \right] + 100z \quad (-) \end{aligned} \quad (82)$$

where the solute designated by, *z*, is a *n*-alkane,  $\text{C}_z\text{H}_{2z+2}$ . Comparing Eq. (81) with Eq. (82) shows that the retention index is proportional to the logarithm of the relative retention of the solute with the paraffin,  $\text{C}_z\text{H}_{2z+2}$ , relative to the logarithm of the relative retention of the paraffins with carbon numbers, *z* and *z* + 1. The advantage of the retention index

is that its temperature dependence is small. Therefore for the determination of the distribution characteristics of a solute the following procedure is recommended:

**Example:** Determination of retention indices and *g-SPOT*-s of a series of solutes in a given solvent as function of temperature.

*Preparation.* Two columns are prepared with a given stationary phase and placed in the oven of the gas chromatograph. Temperature and carrier flow are regulated. The period during which the nominal temperature is constant is called the working period. It is planned to determine data at a series of temperature steps of 15 or 20 °C.

*Experiments.* Regulate the temperature as close as possible to the nominal temperature of the working period. At the beginning and at the end of a working day inject a series of *n*-alkanes and during the working day the solutes planned. Calculate the retention indices of the solutes. Determine the specific retention volume of the *n*-paraffins at beginning and the end of the day. Accept the results of the day if the retention times in the two chromatograms do not differ by more than 1%. After the working period one disposes of the retention indices of all solutes and several results for the specific retention volume of the *n*-alkanes at about the same temperature. After the working period (several days) calculate the *g-SPOT* of the paraffins at the temperature of the working period. The temperature is changed and the procedure repeated until all measurements are made in the planned temperature range. The temperature of the working periods should be changed irregularly (e.g. not ascendent for the whole series).

*Evaluation.* Calculate the *g-SPOT* of *n*-paraffins related to the molal Henry coefficient as function of temperature by regression, using all the results obtained → report the results. The results of solutes other than that of *n*-alkanes are treated in two ways:

- (1) Calculate the retention index of all solutes as a linear function of temperature → report the results (in a few cases the dependence is not linear and a quadratic function must be used).
- (2) For a given solute correct every individual retention index to the adequate nominal temperature with the aid of the temperature dependence of the index (e.g. 149.5 → 150.0 °C). This correction is in general very small, much smaller than the experimental error (less than 0.5 index unit). Transform every individual corrected experimental retention index of the solute point by point to *g-SPOT* with the aid of the *g-SPOT* of the alkane by interpolation (at this stage we dispose of the *g-SPOT* of the alkane). Calculate the temperature dependence for every solute by using all results obtained in the working period → report the results.

*Note:* It is an error to transform points calculated from the linear or quadratic regression of the solute for the calculation of the *g-SPOT* of the solute. In the same train of thought, extrapolated retention indices cannot be transformed to *g-SPOT*-s.

## 4. Examples

### 4.1. Conversion of interaction parameters

All the data needed for the interconversion of interaction parameters related to different distribution coefficients (see Eqs. (64a)–(64c) are summarized in Table 1. The densities

Table 1

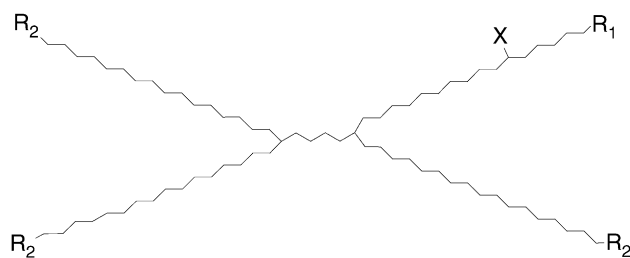
Corrections to add to the interaction parameters related to molal distribution coefficients to give interaction parameters related to molar distribution coefficients with  $T^\dagger = 403.15$  K. The solvents, X/C<sub>78</sub>, are 1:1 (V:V) mixtures

Solvent	$\delta H_{\text{corr}}$ (J mol <sup>-1</sup> )	$\delta S_{\text{corr}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\delta C_{\text{corr}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
C <sub>78</sub>	-1034	-4.721	-5.7
<i>st: C<sub>78</sub></i>	<i>0</i>	<i>0</i>	<i>0</i>
PCI	-1031	-4.522	-5.7
<i>st: C<sub>78</sub></i>	<i>+3</i>	<i>+0.199</i>	<i>+0.0</i>
PCI/C <sub>78</sub>	-1032	-4.622	-5.7
<i>st: C<sub>78</sub></i>	<i>+2</i>	<i>+0.099</i>	<i>0.0</i>
MTF	-1050	-4.541	-5.8
<i>st: C<sub>78</sub></i>	<i>-16</i>	<i>+0.180</i>	<i>-0.1</i>
TTF	-1075	-3.756	-6.4
<i>st: C<sub>78</sub></i>	<i>-41</i>	<i>+0.965</i>	<i>-0.7</i>
TTF/C <sub>78</sub>	-1054	-4.239	-6.1
<i>st: C<sub>78</sub></i>	<i>-20</i>	<i>+0.482</i>	<i>-0.4</i>
TMO	-1062	-4.448	-6.3
<i>st: C<sub>78</sub></i>	<i>-28</i>	<i>+0.273</i>	<i>-0.6</i>
TMO/C <sub>78</sub>	-1048	-4.585	-6.0
<i>st: C<sub>78</sub></i>	<i>-14</i>	<i>+0.136</i>	<i>-0.3</i>
PCN	-1037	-4.609	-5.9
<i>st: C<sub>78</sub></i>	<i>-3</i>	<i>+0.112</i>	<i>-0.2</i>
PCN/C <sub>78</sub>	-1035	-4.665	-5.8
<i>st: C<sub>78</sub></i>	<i>-1</i>	<i>+0.056</i>	<i>-0.1</i>
PSH	-1036	-4.562	-5.8
<i>st: C<sub>78</sub></i>	<i>-2</i>	<i>+0.159</i>	<i>-0.1</i>
PSH/C <sub>78</sub>	-1035	-4.642	-5.8
<i>st: C<sub>78</sub></i>	<i>-1</i>	<i>+0.079</i>	<i>-0.1</i>
POH	-1056	-4.664	-5.7
<i>st: C<sub>78</sub></i>	<i>-22</i>	<i>+0.057</i>	<i>+0.0</i>
POH/C <sub>78</sub>	-1045	-4.693	-5.7
<i>st: C<sub>78</sub></i>	<i>-11</i>	<i>+0.028</i>	<i>+0.0</i>
SOH	-1055	-4.717	-6.2
<i>st: C<sub>78</sub></i>	<i>-21</i>	<i>+0.004</i>	<i>-0.5</i>
SOH/C <sub>78</sub>	-1044	-4.719	-6.0
<i>st: C<sub>78</sub></i>	<i>-10</i>	<i>0.000</i>	<i>-0.3</i>

Corrections to add to interaction parameters of solutes related to Henry coefficients to give interaction parameters related to Ostwald coefficients (see Eqs. (68a)–(68c)).  $T^\dagger = 403.15$  K

	+3351.8	+37.5139	+8.31
<i>st: C<sub>78</sub></i>	<i>0</i>	<i>0</i>	<i>0</i>

The corrections based on the temperature dependence of the density of the stationary phases are calculated with Eq. (63) using data published in refs. [9–13] (see Fig. 3). In italics are given the analogous corrections for the conversion of the molal to the molar relative interaction parameters with paraffin C<sub>78</sub> as reference.



	Polar interacting group(s)	R <sub>1</sub>	R <sub>2</sub>	X	Ref.
C <sub>78</sub>	–	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	H	[9,11]
PCI	Primary chloro	CH <sub>2</sub> Cl	CH <sub>2</sub> CH <sub>3</sub>	H	[11]
MTF	Monotrifluoromethyl	CH <sub>2</sub> CF <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	H	[10]
TTF	Tetrakistrifluoromethyl	CH <sub>2</sub> CF <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	H	[10]
TMO	Tetramethoxy	OCH <sub>3</sub>	OCH <sub>3</sub>	H	[12]
PCN	Primary cyano	CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>3</sub>	H	[12]
PSH	Primary thiol	CH <sub>2</sub> SH	CH <sub>2</sub> CH <sub>3</sub>	H	[12]
POH	Primary alcohol	CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>3</sub>	H	[9]
SOH	Secondary alcohol	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	OH	[13]

Fig. 3. Structure of the nearly isomorphous and nearly isochor solvents [9–13].

of the solvents with the structure shown in Fig. 3 have been determined between 70 and 230 °C (the melting point of the solvents is near 70 °C). It is seen that the corrections for different solvents are very similar implying that the densities of the different solvents are similar and that their temperature dependence is nearly equal. Consequently, the corresponding corrections for the molal/molar conversion of the relative interaction parameters with paraffin C<sub>78</sub> as reference (given in small script) are nearly zero. The converting corrections are independent of the nature of the solute.

The corrections for the conversion of the interaction parameters related to Henry coefficients or Ostwald coefficients are given in Table 1. These corrections are independent both of the solvent and of the solute but depend on the choice of the reference temperature  $T^\dagger$ .

### 4.2. Some experimental values

In a series of publications *g-SPOT*-s related to the molal Henry coefficients of some 150 solutes have been reported on nine nearly isomorphous and nearly isochor solvents [9–13] with structures shown in Fig. 3. The solvents must be isochor and isomorphous for it has been shown that the magnitude of the distribution coefficients seriously depends on the molar volume of the solvent and to a lesser extent on its form [9]. In the cited publications data are related to the molal Henry coefficient given in (cal mol<sup>-1</sup>) which were converted to data related to the same coefficient but expressed in (J mol<sup>-1</sup>) following Eqs. (59a)–(59c). As shown in Fig. 3 the polar solvents resemble the basic alkane C<sub>78</sub>, the difference being that they contain an interacting group, or in the case of weakly interacting groups, four of them.

Table 2

Interaction parameters of *n*-octane and 1-hexanol in alkane C<sub>78</sub> and in the solvent POH (see Fig. 3) related to different distribution coefficients based on experimental data between 80 and 180 °C

	ref/sv	<sup>y</sup> Δ <i>H</i>	<sup>y</sup> Δ <i>S</i>	<sup>y</sup> Δ <i>C</i>
<i>n</i> -Octane				
Related to		(cal mol <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )
<i>g</i> <sup>*(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-8,517	-19.540	+12.3
	<i>Gas/POH</i>	-8,320	-19.297	+11.0
	<i>C</i> <sub>78</sub> / <i>POH</i>	+197	+0.243	-1.3
		(J mol <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )
<i>g</i> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-35,635	-81.864	+51.5
	<i>Gas/POH</i>	-34,811	-80.848	+46.0
	<i>C</i> <sub>78</sub> / <i>POH</i>	+824	+1.016	-5.5
<i>h</i> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-36,669	-86.585	+45.8
	<i>Gas/POH</i>	-35,867	-85.512	+40.3
	<i>C</i> <sub>78</sub> / <i>POH</i>	+802	+1.073	-5.5
<i>κ</i> <sub>D</sub> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-32,283	-44.350	+59.8
	<i>Gas/POH</i>	-31,459	-43.334	+54.3
	<i>C</i> <sub>78</sub> / <i>POH</i>	+824	+1.016	-5.5
<i>K</i> <sub>D</sub> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-33,317	-49.071	+54.1
	<i>Gas/POH</i>	-32,515	-47.998	+48.6
	<i>C</i> <sub>78</sub> / <i>POH</i>	+802	+1.073	-5.5
1-Hexanol				
Related to		(cal mol <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )	(cal mol <sup>-1</sup> K <sup>-1</sup> )
<i>g</i> <sup>*(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-8,295	-18.990	+14.3
	<i>Gas/POH</i>	-10,179	-23.039	+47.3
	<i>C</i> <sub>78</sub> / <i>POH</i>	-1,884	-4.049	+33.0
		(J mol <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )
<i>g</i> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-34,706	-79.563	+59.8
	<i>Gas/POH</i>	-42,589	-96.504	+197.9
	<i>C</i> <sub>78</sub> / <i>POH</i>	-7,883	-16.941	+138.1
<i>h</i> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-35,740	-84.284	+54.1
	<i>Gas/POH</i>	-43,645	-101.168	+192.2
	<i>C</i> <sub>78</sub> / <i>POH</i>	-7,905	-16.884	+138.1
<i>κ</i> <sub>D</sub> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-31,354	-42.049	+68.1
	<i>Gas/POH</i>	-39,237	-58.990	+206.2
	<i>C</i> <sub>78</sub> / <i>POH</i>	-7,883	-16.941	+138.1
<i>K</i> <sub>D</sub> <sup>(sv/g)</sup>	<i>Gas/C</i> <sub>78</sub>	-32,388	-46.770	+62.4
	<i>Gas/POH</i>	-40,293	-63.654	+200.5
	<i>C</i> <sub>78</sub> / <i>POH</i>	-7,905	-16.884	+138.1

In italics are the relative interaction parameters in POH with the ideal dilute solution in alkane C<sub>78</sub> as reference. *T*<sup>†</sup> = 403.15 K.

As first example are listed in Table 2 the interaction parameters of *n*-octane and 1-hexanol in alkane C<sub>78</sub> and in POH related to the molal Henry coefficient given in (cal mol<sup>-1</sup>) with the ideal gas at 1 atm pressure as reference, *g*<sub>*i*</sub><sup>\*(sv/g)</sup>, as reported in ref. [9]. In the following are listed the same data converted to (J mol<sup>-1</sup>) with the ideal gas at 1 bar pressure as reference, *g*<sub>*i*</sub><sup>(sv/g)</sup>, by using Eqs. (59a)–(59c). Finally, are given the converted data related to the Henry and the Ostwald coefficients, respectively, calculated with the corrections given in Table 1.

Table 3 reports interaction parameters related to the molal Henry coefficient of *n*-alkanes and three typical solutes in alkane C<sub>78</sub> determined in a temperature domain of 80–230 °C. In Table 4 are reported data for the calculation of relative interaction parameters of the same solutes related

to the molal Henry coefficient in all polar solvents by electing alkane C<sub>78</sub> as reference solvent. The coefficients for the calculation of *l*-SPOT-s were obtained by subtracting from a given coefficient the corresponding coefficient for alkane C<sub>78</sub> [9–13].

## 5. Final remarks

### 5.1. The interaction parameter set to be preferred

Let us now put forward the question which set of interaction parameters is the right one. From a purist standpoint we can answer this question: the one related to the classical Henry coefficient. This coefficient is practically never used,

because in gas chromatography the molar mass of the solvent is often unknown. Concerning the interaction parameter sets related to the four remaining coefficients the answer is that they are equivalent. The practitioner prefers the molal Ostwald coefficient, because it is equal to the specific retention volume. For the calculation of molar coefficients knowledge of the density of the solvent is necessary.

The differences between the numerical value of interaction parameters related to different distribution coefficients are important, especially between those related to the Henry coefficients and those related to the Ostwald coefficients. However, the corrections are additive and independent of the nature of the solute and nearly independent of the nature of the solvent. Differences between relative interaction parameters related to molal and molar Henry coefficients are in the order of the experimental error.

As a conclusion, substances to be compared must be characterized by interaction parameters referred to the same standard states. Hence, publishing data this relation must be exactly specified and analysing data one must control that the data are homogeneous.

We prefer interaction parameters related to the molal Henry coefficient (listed as examples in Tables 3 and 4). The reason is that these parameters are the closest to those related

to the classical Henry coefficient, two of them,  ${}^g\Delta H_i^{(sv/g)}$  and  ${}^g\Delta C_i^{(sv/g)}$ , being identical. The relationship between the two Henry coefficients in question is (see Eq. (25)):

$$h_i^{(sv/g)} = \frac{g_i^{(sv/g)}}{M_{sv}} \quad (\text{bar}) \quad (83)$$

Consequently, the corresponding  $g$ -SPOT-s are related as:

$$\Delta\mu_i^{(sv/g)} = {}^g\Delta\mu_i^{(sv/g)} - RT \ln(M_{sv}/\text{kg mol}^{-1}) \quad (\text{J mol}^{-1}) \quad (84)$$

Hence, the corresponding interaction parameters are related as follows:

$$\Delta H_i^{(sv/g)}(T^\dagger) \equiv {}^g\Delta H_i^{(sv/g)} \quad (\text{J mol}^{-1}) \quad (85a)$$

$$\Delta S_i^{(sv/g)}(T^\dagger) = {}^g\Delta S_i^{(sv/g)} + R \ln(M_{sv}/\text{kg mol}^{-1}) \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (85b)$$

$$\Delta C_{P,i}^{(sv/g)} \equiv {}^g\Delta C_i^{(sv/g)} \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (85c)$$

The molar mass of the solvents listed in Tables 3 and 4 are near  $1 \text{ kg mol}^{-1}$ , hence the difference between the two sorts of entropic parameters is small. For example:  $R \ln M_{sv} = +0.763 \text{ J mol}^{-1} \text{K}^{-1}$  for  $C_{78}$  and  $+2.258 \text{ J mol}^{-1} \text{K}^{-1}$  for TTF.

## 5.2. Unknown quantity of the solvent

If the quantity of the solvent in the column is unknown, the specific retention volume,  $V_{g,i} = V_{N,i} (\text{cm}^3)/w_{sp} (\text{g}) = \mathfrak{R}T/g_i (\text{cm}^3 \text{g}^{-1} \equiv \text{L kg}^{-1})$  cannot be calculated. We put now forward the question which interaction parameters can be determined if only the net retention volume is known at several temperatures. Combination of Eqs. (35), (51) and (71) results:

$$\begin{aligned} -RT \ln \left( \frac{V_{N,i}}{\mathfrak{R}T} \right) &= RT \ln g_i^{(sv/g)} - RT \ln w_{sp} = {}^g\Delta\mu_i^{(sv/g)} \\ -RT \ln w_{sp} &= {}^g\Delta H_i^{(sv/g)} - T({}^g\Delta S_i^{(sv/g)} + R \ln w_{sp}) \\ + {}^g\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] & \quad (\text{J mol}^{-1}) \quad (86) \end{aligned}$$

Knowledge of the value of this function at more than three temperatures permits determination of the partial molar enthalpy at the reference temperature and the heat capacity of the solute related to the molal Henry coefficient, which are equal to those related to the classical Henry coefficient.

If on the applied stationary phase the  $g$ -SPOT of a solute at one temperature is known, the weight of the stationary phase can be calculated. From Eq. (86) follows that:

$$\ln w_{sp} = \left( \frac{{}^g\Delta\mu_i^{(sv/g)}}{RT} \right) + \ln \left( \frac{V_{N,i}}{\mathfrak{R}T} \right) \quad (\text{J mol}^{-1}) \quad (87)$$

Table 3

Interaction parameters of some solutes in alkane  $C_{78}$  related to the molal Henry coefficient in the temperature range of 70–230 °C with  $T^\dagger = 403.15 \text{ K}$

Solvent	Solute	${}^g\Delta H^{(sv/g)}$ (J mol <sup>-1</sup> )	${}^g\Delta S^{(sv/g)}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	${}^g\Delta C^{(sv/g)}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$C_{78}$ [9,11]	Pentane	-23,041	-67.232	+25.9
	Hexane	-27,217	-71.876	+32.6
	Heptane	-31,451	-76.848	+44.8
	Octane	-35,635	-81.864	+51.5
	Nonane	-39,878	-87.103	+60.2
	Decane	-44,095	-92.303	+66.1
	Undecane	-48,371	-97.688	+79.9
	Dodecane	-52,589	-102.956	+85.8
	Cyclohexane	-28,434	-69.727	+39.3
	1-Cl-hexane	-36,028	-80.584	+50.6
	1-Hexanol	-34,706	-79.563	+59.8
		$\pm 14^*$	$\pm 0.026^*$	$\pm 0.42^*$

Smoothed values of the interaction parameters of  $n$ -alkanes,  $C_nH_{2z+2}$ , in the solvent  $C_{78}$  to obey the function  $a + b z$  for  ${}^g\Delta C$ , and  $a + b z + c z^{-1}$  for  ${}^g\Delta H$  and  ${}^g\Delta S$  (it permits extrapolation of the interaction parameters to higher carbon number alkanes)

Pentane	-23,065 <sub>4169</sub>	-67.136 <sub>4.661</sub>	+26.7 <sub>8.2</sub>
Hexane	-27,234 <sub>4195</sub>	-71.797 <sub>4.907</sub>	+34.9 <sub>8.2</sub>
Heptane	-31,429 <sub>4212</sub>	-76.704 <sub>5.062</sub>	+43.1 <sub>8.2</sub>
Octane	-35,641 <sub>4222</sub>	-81.766 <sub>5.164</sub>	+51.3 <sub>8.2</sub>
Nonane	-39,863 <sub>4230</sub>	-86.930 <sub>5.236</sub>	+59.5 <sub>8.2</sub>
Decane	-44,093 <sub>4236</sub>	-92.166 <sub>5.289</sub>	+67.7 <sub>8.2</sub>
Undecane	-48,329 <sub>4240</sub>	-97.455 <sub>5.328</sub>	+75.9 <sub>8.2</sub>
Dodecane	-52,569 <sub>4242</sub>	-102.783 <sub>5.358</sub>	+84.1 <sub>8.2</sub>
Tridecane	-56,811 <sub>4246</sub>	-108.141 <sub>5.381</sub>	+92.3 <sub>8.2</sub>
Tetradecane	-61,057	-113.522	+100.5

Reference states: ideal gas phase with 1 bar pressure and the 1 molal solution in the alkane. For the structure of the solvents see Fig. 3.

\* Reproducibility at the 95% significance level.

Table 4

Relative interaction parameters of some solutes in solvents isochor with the alkane C<sub>78</sub> related to the molal Henry coefficient in the temperature range of 70–230 °C. with the alkane C<sub>78</sub> as reference and  $T^{\ddagger} = 403.15$  K

Solvent	Solute	${}^g \Delta H^{(sv/C_{78})}$ (J mol <sup>-1</sup> )	${}^g \Delta S^{(sv/C_{78})}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	${}^g \Delta C^{(sv/C_{78})}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
PCI [11]	Pentane	+427	+0.435	+13.0
	Hexane	+439	+0.435	+11.3
	Heptane	+448	+0.435	+9.6
	Octane	+460	+0.435	+7.9
	Nonane	+473	+0.435	+6.3
	Decane	+481	+0.435	+5.0
	Undecane	+490	+0.435	+3.3
	Dodecane	+502	+0.435	+1.7
	Cyclohexane	+418	+0.439	+5.0
	1-Chlorohexane	+176	+0.226	+4.6
	1-Hexanol	-343	-0.678	+11.3
MTF [10]	Pentane	-289	-0.473	-7.1
	Hexane	-259	-0.448	-6.7
	Heptane	-234	-0.423	-6.3
	Octane	-205	-0.397	-5.4
	Nonane	-180	-0.372	-5.0
	Decane	-151	-0.347	-4.2
	Undecane	-121	-0.322	-3.8
	Dodecane	-96	-0.297	-3.3
	Cyclohexane	-301	-0.640	-11.7
	1-Chlorohexane	-531	-0.816	+11.3
	1-Hexanol	-1100	-1.854	+7.9
TTF [10]	Pentane	+205	-0.109	-7.9
	Hexane	+255	-0.109	-7.1
	Heptane	+301	-0.109	-6.7
	Octane	+347	-0.109	-6.3
	Nonane	+393	-0.109	-5.9
	Decane	+444	-0.109	-5.4
	Undecane	+490	-0.109	-5.0
	Dodecane	+536	-0.109	-4.6
	Cyclohexane	+205	-0.632	-10.5
	1-Chlorohexane	-577	-0.979	+9.6
	1-Hexanol	-1732	-3.146	+18.0
TMO [12]	Pentane	+92	-0.431	+4.6
	Hexane	+50	-0.582	+5.0
	Heptane	+4	-0.736	+5.9
	Octane	-42	-0.891	+6.3
	Nonane	-84	-1.042	+7.1
	Decane	-130	-1.197	+7.5
	Undecane	-176	-1.351	+7.9
	Dodecane	-218	-1.502	+8.8
	Cyclohexane	+188	-0.176	+19.7
	1-Chlorohexane	-1209	-2.255	+20.1
	1-Hexanol	-7556	-14.226	+57.7
PCN [12]	Pentane	+477	+0.050	-13.4
	Hexane	+423	-0.121	-12.6
	Heptane	+368	-0.289	-12.1
	Octane	+310	-0.460	-11.3
	Nonane	+255	-0.628	-10.9
	Decane	+201	-0.799	-10.0
	Undecane	+146	-0.967	-9.2
	Dodecane	+88	-1.138	-8.8
	Cyclohexane	+318	-0.310	-13.8
	1-Chlorohexane	-586	-1.268	-13.4
	1-Hexanol	-4489	-8.883	+32.2



Table 4  
(Continued)

Solvent	Solute	${}^g\Delta H^{(sv/C_{78})}$ (J mol <sup>-1</sup> )	${}^g\Delta S^{(sv/C_{78})}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	${}^g\Delta C^{(sv/C_{78})}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
PSH [12]	Pentane	+335	-0.088	+2.5
	Hexane	+372	-0.050	+1.7
	Heptane	+414	-0.013	+0.4
	Octane	+456	+0.029	-0.8
	Nonane	+498	+0.067	-2.1
	Decane	+540	+0.105	-2.9
	Undecane	+577	+0.142	-4.2
	Dodecane	+619	+0.180	-5.4
	Cyclohexane	+209	-0.372	-2.1
	1-Chlorohexane	+276	+0.063	-15.5
POH [9]	1-Hexanol	-381	-1.084	+0.8
	Pentane	+849	+1.184	-3.8
	Hexane	+845	+1.130	-4.6
	Heptane	+837	+1.071	-5.0
	Octane	+824	+1.017	-5.4
	Nonane	+820	+0.962	-6.3
	Decane	+812	+0.904	-6.7
	Undecane	+808	+0.849	-7.1
	Dodecane	+799	+0.791	-7.5
	Cyclohexane	+770	+1.029	-8.8
SOH [13]	1-Chlorohexane	+573	+1.243	-2.9
	1-Hexanol	-7883	-16.941	+138.1
	Pentane	+536	+0.992	+2.9
	Hexane	+565	+1.029	+0.8
	Heptane	+598	+1.079	-1.3
	Octane	+628	+1.117	-3.3
	Nonane	+661	+1.155	-5.4
	Decane	+690	+1.205	-7.5
	Undecane	+720	+1.243	-9.6
	Dodecane	+753	+1.280	-11.7
	Cyclohexane	+565	+1.042	-2.9
	1-Chlorohexane	+163	+0.669	-2.5
	1-Hexanol	-5176	-10.560	+51.9

### 5.3. Unknown quantity of the solvent and unknown flowrate

It is supposed, that the volume between the point of injection and the point of detection,  $V'_\mu$  (cm<sup>3</sup>), is independent of temperature (this is not always true, see ref. [14]). An unretained probe traverses this volume during the time,  $t'_\mu$ . Time and volume are related as:

$$V'_\mu = ct'_{\mu} \quad (\text{cm}^3) \quad (88)$$

where  $ct$ , is a (unknown) constant. The “retention factor”:

$$k_i = \frac{t_{R,i} - t'_\mu}{t'_\mu} = \frac{V_{R,i} - V'_\mu}{V'_\mu} = \frac{V_{N,i}}{V'_\mu} \quad (-) \quad (89)$$

is the net retention of the solute,  $i$ , given in units of the (unknown) volume,  $V'_\mu$ . Hence, the specific retention volume,  $V_{g,i} = k_i V'_\mu$  (cm<sup>3</sup>)/ $w_{sp}$  (g) =  $\Re T/g_i$  (cm<sup>3</sup> g<sup>-1</sup>  $\equiv$  L kg<sup>-1</sup>) cannot be calculated. Combination of Eqs. (35), (51), (71) and

(89) results:

$$\begin{aligned} & -RT \ln \left( \frac{k_i}{\Re T} \right) \\ &= RT \ln g_i^{(sv/g)} - RT \ln \left( \frac{w_{sp}}{V'_\mu} \right) \\ &= {}^g\Delta\mu_i^{(sv/g)} - RT \ln \left( \frac{w_{sp}}{V'_\mu} \right) \\ &= {}^g\Delta H_i^{(sv/g)} - T \left[ {}^g\Delta S_i^{(sv/g)} + R \ln \left( \frac{w_{sp}}{V'_\mu} \right) \right] \\ &+ {}^g\Delta C_i^{(sv/g)} \left[ T - T^\dagger - T \ln \left( \frac{T}{T^\dagger} \right) \right] \quad (\text{J mol}^{-1}) \end{aligned} \quad (90)$$

If on the applied stationary phase the  $g$ -SPOT of any solute at one temperature is known, the value of the factor,  $w_{sp}/V'_\mu$ , can be calculated.

#### 5.4. Final note

There is a principal argument against the use of the “molar” coefficients,  $h_i^{(sv/g)}$  and  $K_{D,i}^{(sv/g)}$ , for the calculation of *g*-SPOT-s. By changing the temperature  $T_1 \rightarrow T_2$  there is loss of solvent (see Fig. 2), i.e., the system is open, contrary to the closed GC-system. In the case of the classical *Henry* coefficient the related interaction parameters are  $\Delta H_i(T^\dagger)$ ,  $\Delta S_i(T^\dagger)$  and  $\Delta C_{P,i}$ , where the subscript, *P* (constant), is true for both, the gas and the solvent phase. The *g*-SPOT related to the molal *Henry* coefficient results,  ${}^g\Delta H_i \equiv \Delta H_i(T^\dagger)$ ,  ${}^g\Delta S_i$  and  ${}^g\Delta C_i \equiv \Delta C_{P,i}$ , a further argument for its use for the determination of interaction parameters. Finally, the interaction parameters related to the molal *Ostwald* coefficient are,  ${}^k\Delta H_i \equiv {}^k\Delta U_i(T^\dagger)$ ,  ${}^k\Delta S_i$  and  ${}^k\Delta C_i \equiv {}^k\Delta C_{V,i}$ , where the subscript, *V* (constant), is true for the gas phase but only approximately true for the solvent phase.

#### Acknowledgements

The authors gratefully acknowledge criticism of the manuscript by Pierre Infelta, Raymond Roulet, Hugo Wyler (Lausanne, Switzerland), Antoine-Michel Siouffi (Aix-Marseille, France), Michel Martin (Paris, France) and Georges Guiochon (Knoxville, USA). One of the authors

(A.D.) is grateful for financial help by the foundation “Pro Arte Chimica Helveto-Pannonica” (Veszprém, Hungary).

#### References

- [1] S.H. Quasim, *SI Units in Engineering and Technology*, Pergamon Press, Oxford, 1977.
- [2] <http://physics.nist.gov/cuu/constants/>.
- [3] IUPAC, *Pure Appl. Chem.* 73 (2001) 969.
- [4] G. Défayes, D.F. Fritz, T. Görner, G. Huber, C. de Reyff, E.sz. Kováts, *J. Chromatogr.* 500 (1990) 139.
- [5] J.R. Conder, C.L. Young, *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1979; see also: R.J. Laub, R.L. Pecsok, *Physicochemical Measurements by Gas Chromatography*, Wiley, New York, 1978.
- [6] A.J.P. Martin, A.T. James, *Biochem. J.* 50 (1952) 679.
- [7] D.F. Fritz, A. Sahil, E.sz. Kováts, *J. Chromatogr.* 186 (1979) 63.
- [8] F. Riedo, E.sz. Kováts, *J. Chromatogr.* 186 (1979) 47.
- [9] K.S. Reddy, J.-Cl. Dutoit, E.sz. Kováts, *J. Chromatogr.* 609 (1992) 229.
- [10] K.S. Reddy, R. Cloux, E.sz. Kováts, *J. Chromatogr. A* 673 (1994) 181.
- [11] G. Défayes, K.S. Reddy, A. Dallos, E.sz. Kováts, *J. Chromatogr. A* 699 (1995) 131.
- [12] K.S. Reddy, R. Cloux, E.sz. Kováts, *J. Chromatogr. A* 704 (1995) 387.
- [13] A. Dallos, A. Sisak, Z. Kulcsár, E.sz. Kováts, *J. Chromatogr. A* 904 (2000) 211.
- [14] F. Riedo, D. Fritz, G. Tarján, E.sz. Kováts, *J. Chromatogr.* 126 (1976) 63.