

**TEMPERATURE DEPENDENCE OF KOVÁTS INDICES
IN GAS CHROMATOGRAPHY.
EXPLANATION OF EMPIRICAL CONSTANTS
BY USE OF TRANSITION-STATE THEORY**

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SUMMARY

The temperature dependence of Kováts indices is best described by use of the empirical equation $I = A + B/T + C \ln T$ [1]. This paper discusses the physical significance of the equation constants linked to the $1/T$ and $\ln T$ terms. The explanation presented here is based on transition state theory, i.e. the activation energy assumed to be associated with the solvation process. Because the literature contains no measured activation energy data for the solvation process, elucidation of the physical meaning of other terms might be an acceptable alternative. The Gibbs free energy for one methylene unit can be calculated and compared with literature values. The activation energy of the solvation process changes systematically.

INTRODUCTION

The temperature dependence of Kováts retention indices can be expressed by use of a simple linear equation or, for wide temperature range, by use of an Antoine-type reciprocal equation [2]. Tudor reinvestigated the temperature dependence of Kováts indices and examined linear hyperbolic equations [3–5]. Minima in the temperature dependence have recently been observed [1,6]. The new equation describing the minimum [1]:

$$I = A + \frac{B}{T_c} + C \ln T_c \quad (1)$$

has, however, not been explained. Our objective in this work was, therefore, is to attribute physical meaning to the equation constants (regression constants) A , B , and C .

THEORY

Although the working temperature (T) at which GC analysis is conducted is the key factor determining the overall separation time and governing separation performance, the relationship between the working temperature of the GC column and the Kováts retention index, I , which passes through a minimum, has not been interpreted physicochemically. It is, therefore, expedient to attribute thermodynamic significance to the minimum in the empirical relationship between I and T .

The commonly accepted thermodynamic description of the Kováts retention index for the i th solute, $I_{(i)}$, is [7–10]:

$$\frac{I_{(i)}}{100} = \frac{\ln K_{p(i)}}{\ln K_{p(\text{CH}_2)}} \quad (2)$$

where $K_{p(i)}$ is the thermodynamic constant of partitioning of the i th solute between the mobile and the stationary phases and $K_{p\text{CH}_2}$ is the analogous thermodynamic constant for partitioning of one methylene group of an n -alkane. Although, strictly speaking, $K_{p\text{CH}_2}$ depends on temperature, as an approximation we can use a mean value for the given range of temperatures. Consequently, $K_{p\text{CH}_2}$ and $\Delta\mu_{p\text{CH}_2}$ denote average values which are related by the equation:

$$\Delta\mu_{p(\text{CH}_2)} = -RT_{\text{mean}} \ln K_{p(\text{CH}_2)} \quad (3)$$

Here we present a possible explanation of temperature dependence of Kováts indices. For simplicity it is called a kinetic explanation. This kinetic explanation has already been given elsewhere [11]; here we recapitulate the most important parts only.

(i) The process of establishing thermodynamic equilibrium between the solute in the mobile (m) and the stationary (s) phases can be well approximated by the solution–vaporization process:



which apparently is a purely physical phenomenon.

(ii) We can also attribute the usual chemical kinetic measures to this process. The temperature dependence of the reaction rate constant is given by the Eyring–Polanyi equation [12,13]:

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (5)$$

where k , \mathbf{k} , and \mathbf{h} are the rate constant of solvation, the Boltzmann constant, and the Planck quantum constant, respectively, and ΔH^\ddagger and ΔS^\ddagger are the enthalpy and the entropy of activation, respectively, for the solution process.

The Brønsted relationship [14] binds together the rate constant and the equilibrium constant of solvation (i.e. the partitioning constant). It is rightfully regarded as the first linear free energy relationship ever established. It is valid for similar compounds, compound classes, and congener series of compounds also. Its simplest form is given below, adapted to the gas-chromatographic retention process (under the aforementioned conditions, which enable consideration of solute retention as equivalent to the solution \leftrightarrow vaporization process):

$$k = \varepsilon K_{p(i)} \quad (6)$$

where k is the rate constant of the solution process, ε is the Brønsted constant (i.e. the rate constant of the reverse process, vaporization), and $K_{p(i)}$ is the equilibrium constant of the solute partitioning between the mobile and the stationary phases. Combining eqs (5) and (6) with eq. (3), we again arrive at eq. (1), where:

$$A = 100 \left(\ln \frac{\mathbf{k}}{\varepsilon \mathbf{h}} + \frac{\Delta S^\ddagger}{R} \right) / \ln K_{p(CH_2)} \quad (7)$$

$$B = -\frac{100 \Delta H^\ddagger}{R \ln K_{p(CH_2)}} \quad (8)$$

$$C = \frac{100}{\ln K_{p(CH_2)}} \quad (9)$$

Here the average value of $\Delta \mu_{pCH_2}$ can be calculated from the constant C . The ratio of B to C provides the activation enthalpy of solution.

RESULTS AND DISCUSSION

Chemical potentials for one methylene unit and activation enthalpies of solution calculated from the physical meaning of the equation constants of the model $I = A + B/T + C \ln T$ are summarized in Tables I and II. The third and fifth columns in Table I contain thermodynamic quantities relating to vaporization, obtained by use of Trouton's constant. The value of $\Delta\mu_{\text{vap}}$ is almost always negative, convincing evidence that our explanation is physicochemically sound. Table II contains results from statistical fitting for ketones and aldehydes not included in Table I.

Table I

Chemical potentials for one methylene unit and activation enthalpy of solution calculated from the model $I = A + B/T + C \ln T$

	CNo ^a	ΔH_{vap} (J mol ⁻¹) ^b	$T_{(\text{mean})}$ (K) ^c	$\Delta\mu_{\text{vap}}$ (J mol ⁻¹) ^d	$\Delta\mu_{\text{CH}_2 \text{ kinet}}$ (J mol ⁻¹) ^e	ΔH^\ddagger (J mol ⁻¹) ^f
Acetone	3	23880	331.9	-4331.5	-2197	-2863
Butanone	4	27500	331.9	-711.5	-3360	-2741
Pentan-2-one	5	31050	337.4	2367.6	-3141	-2634
Hexan-2-one	6	35850	337.4	7167.6	-2606	-2591
Acetaldehyde	2	17860	331.9	-10352	-1257	-2914
Propanal	3	22930	331.9	-5281.5	-3038	-2805
Isobutanal	4	26110	334.8	-2349.7	-2588	-2503
Butanal	4	27240	334.8	-1219.7	-3789	-2410

^a CNo – number of carbon atoms

^b $\Delta H_{\text{vap}} = -\Delta H_{\text{sol}}$ values from the literature [20], measured independently

^c $T_{(\text{mean})}$ – average measurement temperatures

^d $\Delta\mu_{\text{vap}}$ – free energy of vaporization; $\Delta\mu_{\text{vap}} = \Delta H_{\text{vap}} - T\Delta S_{\text{vap}}$, where ΔS_{vap} is Trouton's constant, 85 J mol⁻¹ K⁻¹

^e $\Delta\mu_{\text{CH}_2}$ was calculated from fitted constant C by use of eqs (3) and (9)

^f ΔH^\ddagger was calculated from fitted constant B by use of eqs (8) and (9)

Because activation energy data attributable to the solvation process have not yet been published, it is impossible to compare the activation energy measured in this study with literature values. There are, however, indications that these activation energy values are realistic. The magnitude of the activation energy is smaller than for chemical reactions, as expected – solution is a physicochemical process. Results from regression analysis reveal that numerical values of A (eq. 1) become more positive as the

Table II

Chemical potentials of one methylene unit and activation enthalpy of solution calculated from the model $I = A + B/T + C \ln T$

	A^a	B^a	C^a	R^b	F^b	S^b	$\Delta\mu_{\text{CH}_2}$ (J mol ⁻¹) ^c	ΔH^\ddagger (J mol ⁻¹) ^d
Pentan-3-one	-231.6	43850	133.5	0.9877	39.95	0.132	-21382	-2732
Butan-2-one, 3-methyl	-71.61	31280	106.4	0.9991	568.4	0.0808	-2682	-2445
Hexan-3-one	8.611	35380	111.8	0.9990	496.2	0.0503	-2552	-2631
Pentan-2-one, 4-methyl	-107.3	37350	123.2	0.9993	706.8	0.0685	-2316	-2521
Butan-3-one, 2,2-dimethyl	-251.0	38340	142.6	0.9995	943.6	0.129	-2000	-2235
Pentan-2-one, 3-methyl	-258.9	41220	149.7	0.9999	4534	0.0560	-1906	-2290
Pentan-3-one, 2,4-dimethyl	-71.99	34150	128.8	0.9998	2760	0.0712	-2216	-2205
Butanal, 3-methyl	110.6	19600	80.26	0.9981	262.7	0.183	-3555	-2030
Butanal, 2-methyl	10.61	24490	0.129	0.9992	638.8	0.129	-2949	-2105
Pentanal	44.66	27090	94.48	0.9997	1928	0.0450	-3020	-2384
Propanal, 2,2-dimethyl	168.2	13750	64.21	0.9992	635.5	0.124	-4443	-1781
Hexanal	-218.0	44690	148.2	0.9999	4934	0.0323	-1926	-2508
Butanal, 2-ethyl	-272.7	40060	154.1	0.9998	2567	0.0946	-1851	-2161
Butanal, 3,3-dimethyl	-570.9	50750	190.9	1.0000	15560	0.0440	-1495	-2210

^a A , B , and C are fitted terms in the model $I = A + B/T + C \ln T$ [1]

^b R , F , and S are multiple correlation coefficients, Fisher statistics, and residual error, respectively [1]

^c $\Delta\mu_{\text{CH}_2}$ was calculated from fitted constant C by use of eqs (3) and (9)

^d ΔH^\ddagger was calculated from fitted constant B by use of eqs (8) and (9)

nature of the aliphatic chain becomes increasingly apolar (which seems generally correct). ΔH^\ddagger was, moreover, determined from the equation constants B and C . Although, if we calculate values of B or C for increasing molecular mass, we see no systematic change, the activation energy changes in one direction systematically. Interesting tendencies can be observed. Activation energies for ketones are always higher than those for the corresponding aldehydes, and branching causes a decrease in the activation energy values. These tendencies are illustrated in Figs 1 and 2.

Verification of the physical meaning might be completed by using the standard chemical potential of partitioning of one methylene group ($>\text{CH}_2$) of an n -alkane between the mobile and stationary phases ($\Delta\mu_{(\text{CH}_2)}$). $\Delta\mu_{(\text{CH}_2)}$ depends on the stationary phase and on temperature, and reliable values can be found in the literature. Figure 3 shows that $\Delta\mu_{(\text{CH}_2)}$ values determined from the temperature dependence of Kováts indices for indivi-

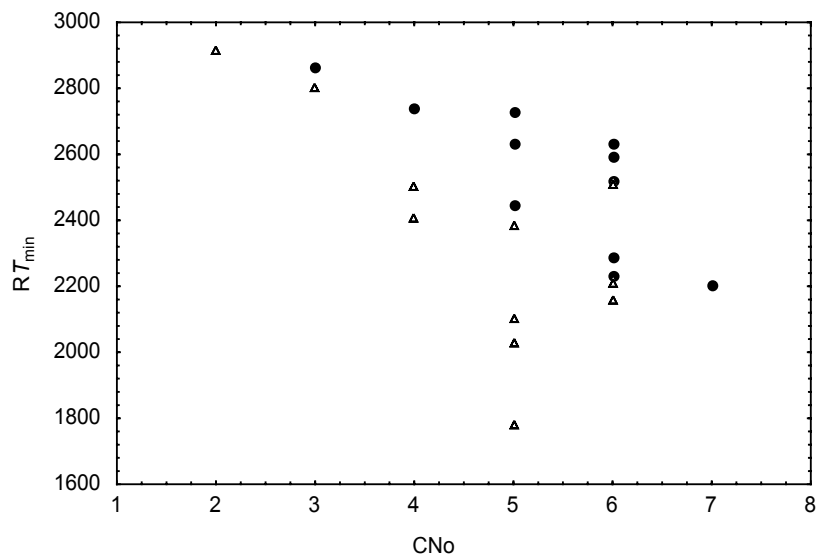


Fig. 1

Dependence on carbon atom number of activation enthalpy of solution for ketones (●) and aldehydes (Δ) (data from Tables I and II)

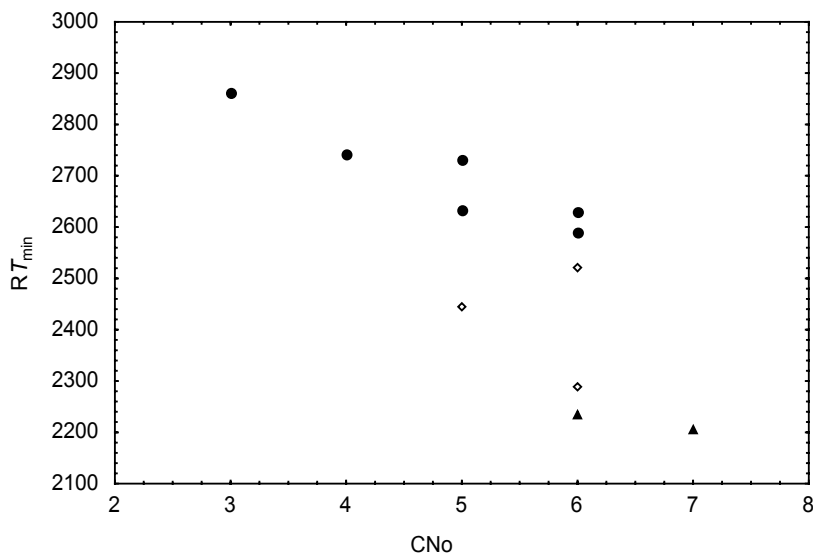


Fig. 2

Dependence on carbon atom number of activation enthalpy of solution for normal (●), branched (◆), and twice branched (▲) ketones (data from Tables I and II)

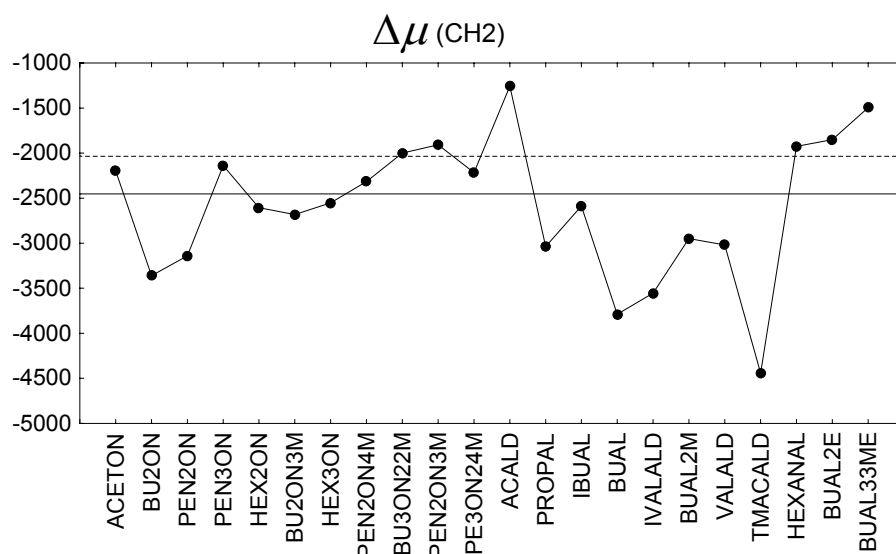


Fig. 3

The chemical potential for partitioning of one methylene unit ($\Delta\mu_{\text{CH}_2}$) from eqs (3) and (9). Dotted and solid lines represent values from Refs [15] and [21], respectively

dual oxo compounds oscillate around the literature values. The average value of $\Delta\mu_{\text{CH}_2}$ is -2750 J mol^{-1} (at 340 K), very close to the literature value of -2160 J mol^{-1} determined for the same stationary phase by means of a completely independent measurement involving *n*-alkanes [21].

Purely formally, eq. (1) is fully analogous with the boiling point-dependence of relative retention data [8,15,16], if the boiling point of the solute replaces the isothermal column temperature in the respective equation. By analogy, perhaps it should be remembered that attribution of physical meaning to the equation constants in an equation extended by the logarithm of the *boiling point term* has been equally unsuccessful for polar and non-polar stationary phases. For a column designed specially for separation of oxo compounds (DB-210), however, it proved possible to determine the chemical potential of partitioning for one methylene unit ($\Delta\mu_{\text{CH}_2}$) from the Kováts retention index – boiling point correlation depended on assumption of the applicability of the Trouton–Hildebrand–Everett rule [9].

The thermodynamic quantities enthalpy and entropy of solution are also temperature-dependent. Because we neglected the temperature depen-

dence of the molar heat capacity, however, the approach presented can be regarded as an approximation only. Because of experimental difficulties, retention measurements can be obtained in narrow temperature ranges only. Authors often state that the narrow temperature interval justifies the assumption that the thermodynamic quantities are independent of temperature [2,17]. Other examinations suggest there is insufficient information; it might be necessary to take into the account the temperature dependence of molar heat capacities also [18,19].

Hennig and Engewald [6] observed a similar distortion (minimum) of the Kováts indices as a function of temperature for alcohols and phenols as the compounds on an apolar stationary phase (HP-5). This distortion was because of adsorption effects, although no quantitative evaluation was given. Our activation energy term must not be confused with the heat of adsorption in gas–solid chromatography – the heat of adsorption is at least one order of magnitude greater [22].

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