

## TEMPERATURE DEPENDENCE OF THE HEIGHT EQUIVALENT TO A THEORETICAL PLATE

TOMIHITO KAMBARA AND HIROSHI KODAMA

*Department of Chemistry, Hokkaido University, Sapporo (Japan)*

(Received May 5th, 1964)

## INTRODUCTION

The height equivalent to a theoretical plate (HETP) represents, as is well known, the column efficiency in chromatographic separation. On the basis of the theory of LAPIDUS AND AMUNDSON<sup>1</sup>, VAN DEEMTER *et al.*<sup>2</sup> derived a famous equation of the following form:

$$H = A + \frac{B}{u} + Cu \quad (1)$$

In this equation  $H$  is the HETP and  $u$  the linear velocity of carrier gas.

KIESELBACH<sup>3</sup> and JONES<sup>4</sup> presented modified theories, and DE WET<sup>5</sup> found a hyperbolic relationship between HETP and temperature, for the elucidation of which he postulated that the diffusion constants in the gaseous and liquid phases are proportional to the absolute temperature and the partition coefficient  $K$  is inversely proportional thereto, resulting in the following expression:

$$H = A + B_3T + \frac{C_4}{T}$$

DUFFIELD<sup>6</sup> varied the linear velocity and found that the third term in the right-hand side of eqn. (1) increased.

In the present study it was deduced from the VAN DEEMTER theory<sup>2</sup> that the logarithm of HETP, and hence the logarithm of the plate number of a given column under certain conditions, varies linearly with the reciprocal of the absolute temperature.

## THEORETICAL CONSIDERATION

LAPIDUS AND AMUNDSON<sup>1</sup>, in 1952, presented a system of partial differential equations, in which diffusion, convection and the kinetics of dissolution into stationary phase and evaporation therefrom are considered mathematically. Their solution, however, was too complicated to be applied to the practical problems, and later VAN DEEMTER *et al.*<sup>2</sup> transformed it into a convenient form of the Gaussian distribution. Namely, it is shown that the outlet concentration is:

$$C_g = \frac{\beta t_0 c_0}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} \exp \left\{ -\frac{\left(t - \frac{L}{\beta u}\right)^2}{\frac{2}{\beta^2}(\sigma_1^2 + \sigma_2^2)} \right\} \quad (2)$$

where  $t$  is the time,  $L$  the column length, and

$$\frac{1}{\beta} = 1 + \frac{F_l}{KF_g} \quad (3)$$

where  $F_g$  and  $F_l$  are the cross-sectional fractions of the gaseous and liquid phases, respectively, and  $K$  is the ratio of the concentration in the gaseous phase to that in the stationary liquid phase at equilibrium. It is considered that a pulse of duration  $t_0$  and concentration  $c_0$  is injected into the column inlet. The variances  $\sigma_1^2$  and  $\sigma_2^2$  are given by:

$$\sigma_1^2 = 2 \frac{D_g L}{u^3} \quad (4)$$

and

$$\sigma_2^2 = 2 \beta^2 \frac{F_l^2 L}{\alpha F_g K^2 u} \quad (5)$$

where  $\alpha$  is the rate constant of dissolution from gaseous into liquid phase and  $D_g$  the diffusion constant in the gaseous phase.

It can easily be shown that the retention time  $t_R$  is given by

$$t_R = \frac{L}{\beta u} \quad (6)$$

The number of plates  $n$  is given by

$$n = \frac{L}{H} = \frac{t_R^2}{\sigma_1^2 + \sigma_2^2} \quad (7)$$

We will discuss the characteristics of eqn. (7) in two extreme cases.

*At low temperatures*

It is seen that in this case:

$$K \longrightarrow 0 \quad \text{and} \quad \frac{1}{\beta} \longrightarrow \frac{F_l}{KF_g} \quad (8)$$

so that the relation

$$\sigma_2^2 \gg \sigma_1^2$$

holds approximately. Hence, it follows that

$$n = \frac{\left(\frac{L}{\beta u}\right)^2}{\left(\frac{\sigma_2}{\beta}\right)^2} = \frac{L \cdot \alpha}{2 \cdot u \cdot F_g} \quad (9)$$

The rate constant of dissolution or adsorption  $\alpha$  may be expressed in the form:

$$\alpha = \alpha_0 \cdot \exp\left(\frac{-\Delta H_1}{RT}\right) \quad (10)$$

where  $\Delta H_1$  is the activation heat of the process. It can therefore be derived that

$$\log n = \log \frac{L \cdot \alpha_0}{2 \cdot u \cdot F_0} - \frac{\Delta H_1}{2.303 RT} \quad (11)$$

*At high temperatures*

In this case:

$$K \longrightarrow \infty \quad \text{and} \quad \beta \longrightarrow 1 \quad (12)$$

so that

$$\sigma_1^2 \gg \sigma_2^2 = 0.$$

Hence, it is seen that

$$n = \frac{t_R^2}{\sigma_1^2} = \frac{L \cdot u}{2 \cdot D} \quad (13)$$

On the other hand, one may write:

$$D = D_0 \cdot \exp\left(\frac{-\Delta H_2}{RT}\right) \quad (14)$$

Thus, it is found that

$$\log n = \log \frac{L \cdot u}{2 \cdot D_0} - \frac{\Delta H_2}{2.303 RT} \quad (15)$$

or

$$\log H = \log \frac{2 \cdot D_0}{u} + \frac{\Delta H_2}{2.303 RT} \quad (16)$$

## EXPERIMENTAL

The benzene, toluene, isopropyl alcohol and ethyl alcohol used were all the reagent grade. The gas chromatograph was a Hitachi apparatus (Type KGL-24A). The column was 3 m long and 4 mm in diameter and the 10% Apiezon grease L (40-60 mesh) served as the stationary phase. Helium was used as the carrier gas, and the pressure difference between the inlet and the outlet was maintained at 0.4 kg/sq. cm throughout the measurement. The amount of sample injected was always kept to 5  $\mu$ l.

The variation of the linear velocity with temperature offers a complicated problem, but in this study it is assumed that the linear velocity of carrier gas remains approximately constant owing to the constant pressure difference. The change in the flow rate of gas volume expressed in mole/sec is measured and given in Fig. 1.

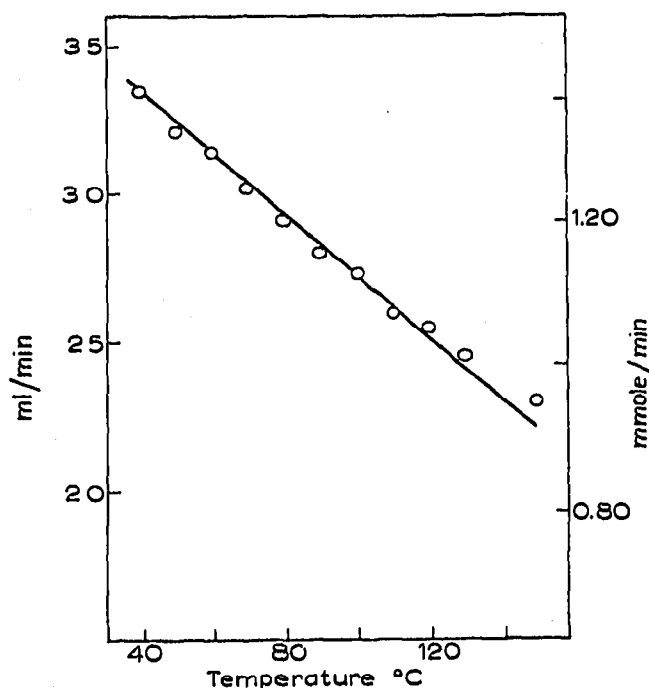


Fig. 1. Variation of the flow rate of helium carrier gas with temperature measured at  $22^\circ \pm 1^\circ$  and 1 atm at the column outlet. Under these conditions the logarithm of the flow rate varied only slightly.

## RESULTS AND DISCUSSION

Some examples of the gas chromatograms recorded are shown in Fig. 2. It is found that with the increasing temperature the retention time becomes shorter and the peak first becomes sharper and then again broader.

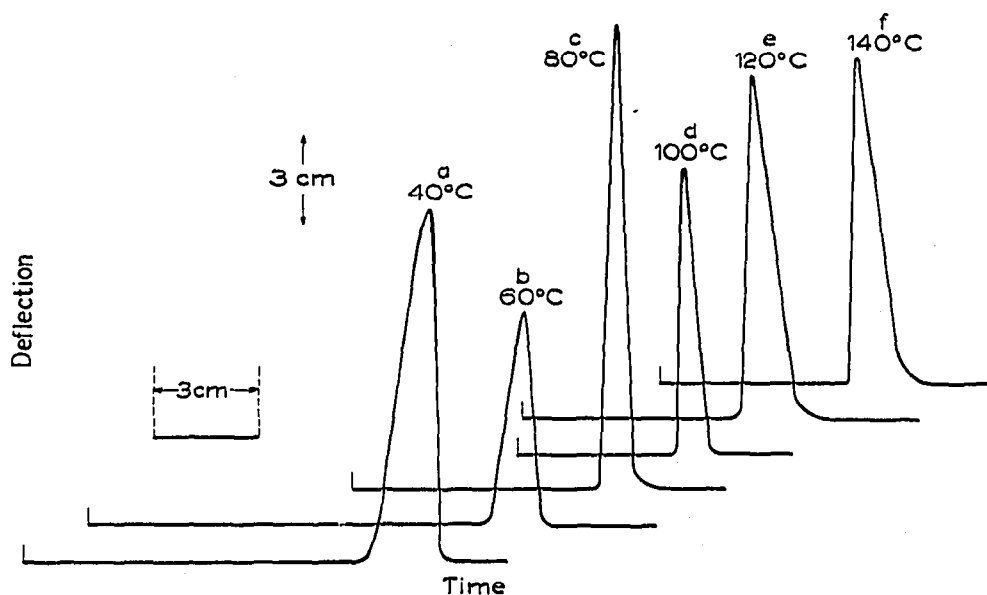
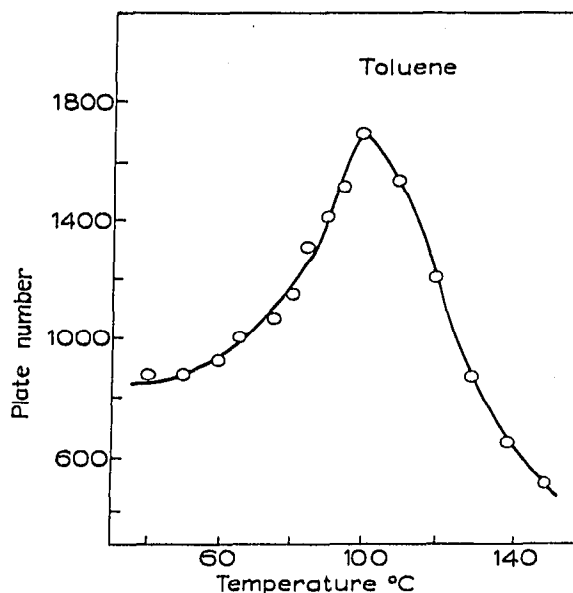
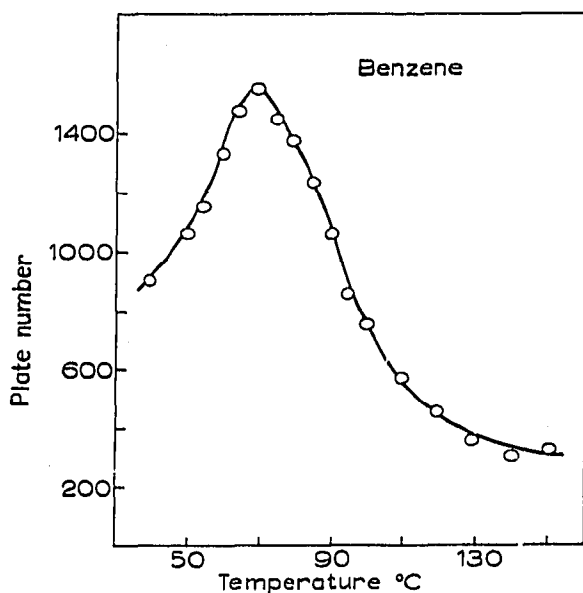


Fig. 2. Gas chromatograms of benzene at various temperatures. Recorder sensitivity (full-scale 23 cm) and chart speed are: (a) 8 mV,  $0.5 \text{ cm min}^{-1}$ ; (b) 32 mV,  $1.0 \text{ cm min}^{-1}$ ; (c) 32 mV,  $1.0 \text{ cm min}^{-1}$ ; (d) 64 mV,  $1.0 \text{ cm min}^{-1}$ ; (e) 64 mV,  $2.0 \text{ cm min}^{-1}$ ; (f) 64 mV,  $2.0 \text{ cm min}^{-1}$ .



Figs. 3 and 4. Variation of plate number with temperature for benzene and toluene.

The number of plates was obtained by means of the equation:

$$n = 5.55 \left( \frac{t_R}{w_h} \right)^2 \quad (17)$$

where  $w_h$  is the half-width of the peak<sup>7,8</sup>. The variation of the number of plates with the temperature is shown in Table I and Figs. 3 and 4.

The logarithm of the plate number plotted against the reciprocal of the absolute temperature is shown in Fig. 5, from which one can easily find good linear

TABLE I

MEASUREMENT OF PLATE NUMBER AND RETENTION VOLUME

Column temperature (°C)	$t/T \times 10^3$	Benzene		Toluene	
		$\log n$	$\log V_R$	$\log n$	$\log V_R$
40	3.19	2.95	3.88	2.95	4.36
50	3.11	3.03	3.73	2.94	4.17
55	3.05	3.06	3.67	—	—
60	3.00	3.12	3.59	2.97	4.02
65	2.96	3.16	3.53	3.00	3.94
70	2.92	3.19	3.46	—	—
75	2.87	3.16	3.38	3.04	3.78
80	2.83	3.14	3.33	3.06	3.72
85	2.79	3.09	3.25	3.11	3.63
90	2.75	3.03	3.21	3.15	3.58
95	2.72	2.92	3.14	3.18	3.49
100	2.68	2.87	3.10	3.23	3.45
110	2.61	2.75	3.00	3.18	3.32
120	2.54	2.66	2.93	3.09	3.20
130	2.48	2.55	2.88	2.94	3.12
140	2.42	2.49	2.78	2.81	3.01
150	2.37	2.51	2.77	2.71	2.95

relationships indicating the essential validity of the present theoretical considerations.

The linear relationship between the  $\log t_R$  and  $1/T$  has been known for a long time, and is also given in Fig. 5. This would support the good control in the experimental work in the present measurement.

Compared with the theories proposed by DE WET<sup>5</sup> and DUFFIELD<sup>6</sup>, the present study elucidates the temperature dependence of HETP, or of plate number in gas chromatography, more elegantly and reasonably and on the basis of sounder physico-chemical considerations.

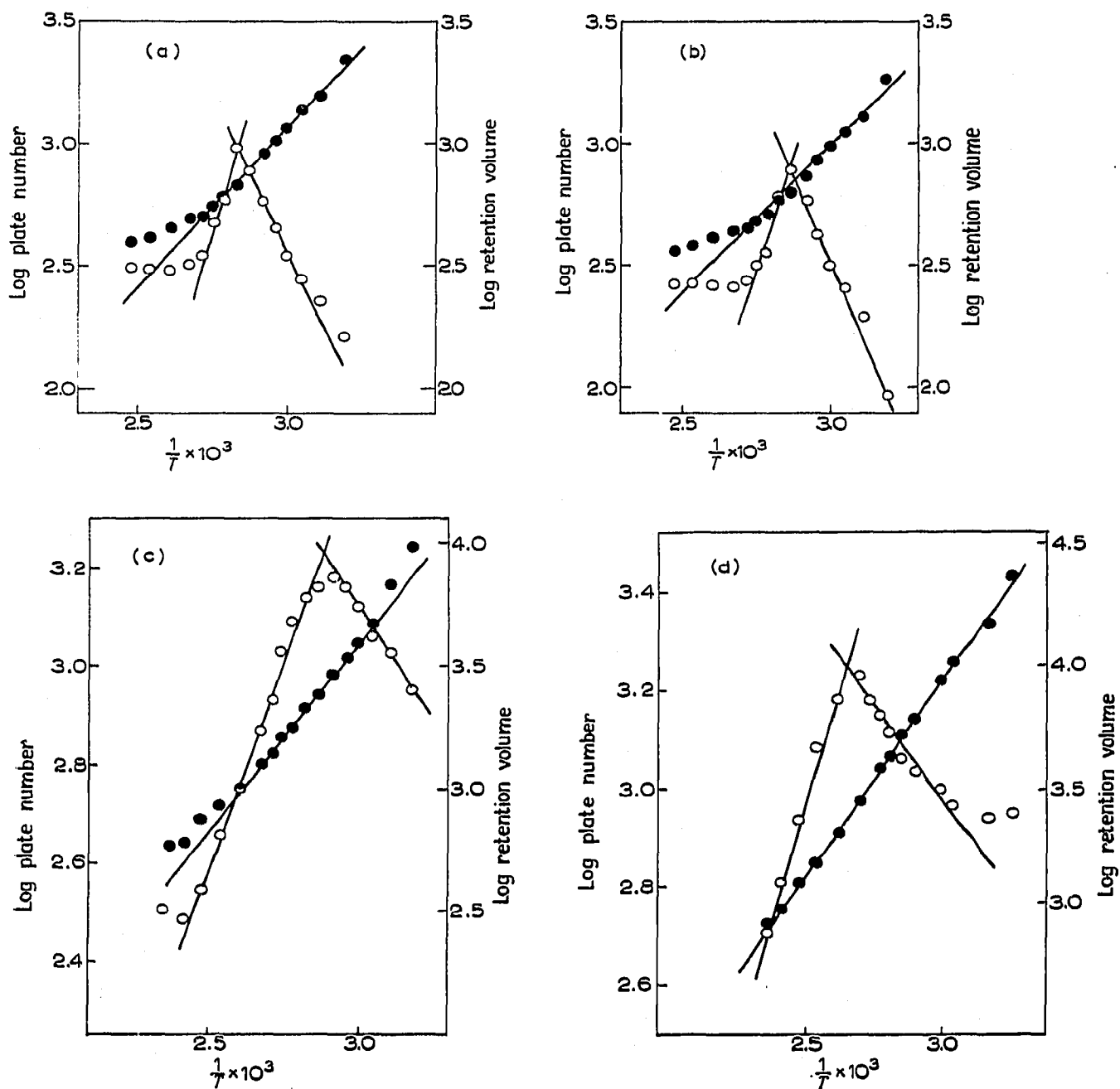


Fig. 5. Plots of  $\log n$  vs.  $1/T$  (shown by open circles).  $\log t_R$  is also plotted for comparison (shown by full circles). (a) Isopropyl alcohol; (b) ethyl alcohol; (c) benzene; (d) toluene.

## SUMMARY

It was predicted theoretically that the plate number of a given column varies with temperature. From the VAN DEEMTER theory<sup>2</sup> it was shown that the logarithm of the plate number, or of HETP, plotted against the reciprocal of the absolute temperature gives two straight lines. This prediction was experimentally confirmed and it was found that each column shows the maximum plate number at a temperature near the boiling point of the sample.

## REFERENCES

- 1 L. LAPIDUS AND N. R. AMUNDSON, *J. Phys. Chem.*, 56 (1952) 984.
- 2 J. J. VAN DEEMTER, F. J. ZUIDERWEG AND A. KLINKENBERG, *Chem. Eng. Sci.*, 5 (1956) 271.
- 3 R. KIESELBACH, *Anal. Chem.*, 33 (1961) 23.
- 4 W. L. JONES, *Anal. Chem.*, 33 (1961) 829.
- 5 W. J. DE WET, *Anal. Chem.*, 30 (1958) 325.
- 6 J. J. DUFFIELD AND L. B. ROGERS, *Anal. Chem.*, 32 (1960) 341.
- 7 H. PURNELL, *Gas Chromatography*, Wiley, New York, 1962, p. 105.
- 8 A. B. LITTLEWOOD, *Gas Chromatography*, Academic Press, New York, 1962, p. 131.

*J. Chromatog.*, 17 (1965) 66-72