diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Coefficients in Solid-State Diffusion by Inverse Gas Chromatography

Assimina V. Dremetsika [1], *Panayotis A. Siskos* [1], *Nicholas A. Katsanos* [2]

[1] University of Athens, Department of Chemistry, Analytical Chemistry Laboratory, 157 71 Zografos, Athens, Greece, e-mail: dremetsika@chem.uoa.gr , siskos@chem.uoa.gr
[2] University of Patras, Department of Chemistry, Physical Chemistry Laboratory,
265 04 Patras, Greece

1. Introduction

The new inverse gas chromatography methodology of Reversed-Flow Gas Chromatography (RF-GC) has been applied to measure diffusion coefficients (D_1) of gases and volatile liquids in porous solids, together with the total overall rate constant of transference $k=k_R+k_2$ onto the solid surface, where k_R is the adsorption/desorption rate constant on the solid adsorbent, and k_2 a catalytic or other rate constant [1]. The method was applied here to formic and acetic acids diffusing into marble and solid metals at various temperatures.

2. Experimental

2.1 Methodology

The experimental arrangement can be found in a recent review [2] or in a book [3]. It consists of a T shape glass or steel tube of ¼ inch chromatographic column. The lower end of the vertical tube contains a small amount of the solid under study, while the horizontal tube is connected to the detector and the carrier gas through a four-port gas sampling valve.

The diffusing substance is injected (1 μl of liquid) into the T tube at its lower end, and the four-port valve is connected in such way, that the carrier gas passes through the horizontal part of the T tube before flowing through the chromatographic detector. By turning the valve from one position to the other, one causes a reversal in the flow direction of the carrier gas lasting only 5-60 s. Shortly after the reversal, a usual recording system connected to the detector plots a narrow symmetrical extra peak of the injected solute, sitting on the otherwise long asymmetrical elution curve. This is repeated many times producing a long series of such narrow sample peaks. An example can be found in Fig. 2 of Ref. [2]. From these sample peaks, obtained under various conditions, several physicochemical parameters can be determined [2, 3]. All are based on the height H of the sample peaks expressed as sum of three exponential functions of time t:

$$H^{1/M} = \sum_i A_i \exp\left(B_i t\right) \tag{1}$$

where $i = 1\text{-}3$, M is the known response factor of the detector used (M=1 for flame ionization detector), and A_i, B_i are functions of the physicochemical quantities pertaining to the various phenomena occuring in the solid bed region. As mentioned in the introduction, the diffusion coefficient (D_1) of gases in porous solids and the total rate constant of transference (k) onto the solid surface can be determined from the A_i and B_i values of Eq.(1), as reported analytically in Ref. [1]. It is to be noted that the probable errors of the above quantities are determined for the first time by inverse gas chromatography.

2.2. Results and Discussion

The methodology briefly described above was applied to Penteli marble and to some common metals for the diffusion into them of formic and acetic acid, which are two common air pollutants acting on ancient art objects. The results are listed in the following Table 1.

Table 1: Diffusion coefficient (D_1) and total rate constant of transference (k) of formic and acetic acid in Penteli marble and three metals in various temperatures

Acid	Solid	Temp./K	10^4 k/s^{-1}	$10^3 D_1$/cm^{2}s^{-1}
Formic	marble	373.2	9.87±0.71	5.63±0.06
Formic	marble	423.2	22.52±2.91	7.04±0.71
Formic	iron	393.2	39.36±1.36	5.52±0.42
Formic	iron	423.2	22.56±4.72	6.84±0.17
Formic	copper	393.2	1.94±0.44	11.22±0.18
Formic	lead	393.2	9.39±2.40	9.43±0.63
Formic	lead	423.2	17.3±0.64	10.37±0.35
Acetic	marble	373.2	11.51±0.39	9.00±0.07
Acetic	marble	393.2	14.21±0.80	9.26±0.08
Acetic	iron	393.2	8.34±1.22	7.60±0.58
Acetic	iron	423.2	29.38±11.3	9.72±0.96
Acetic	copper	423.2	9.02±0.52	9.39±0.18
Acetic	lead	393.2	2.61±1.53	4.54±0.02
Acetic	lead	423.2	5.65±0.44	8.05±0.24

3. Conclusion

Using a simple experimental arrangement, important quantities referring to the damage of solid pieces of traditional art by organic acid air pollutants can be quantitatively measured. The results can lead to important actions for protection of the art pieces from acid atmospheric damage.

References

[1] N. A. Katsanos, N. Bakaoukas, A. Koliadima, G. Karaiskakis, and A. Jannussis, J. Phys. Chem. B (2005) In press.

[2] N. A. Katsanos, J. Chromatogr. A 1037 (2004) 125.

[3] N. A. Katsanos and G. Karaiskakis, Time-Resolved Inverse Gas Chromatography, HNB Publishing, New York, 2004.