

CONTRIBUTION TO THE MECHANISM OF DETERIORATION OF MATERIALS IN MUSEUMS BY KINETIC STUDIES ON ATMOSPHERIC CHEMISTRY

F. Roubani-Kalantzopoulou, E. Kalogirou and A. Kalantzopoulos

Department of Chemical Engineering, Technical University of Athens, 157 80 Zografou, Greece

E. Iliopoulou, Ch. Abatsoglou and N. A. Katsanos

Physical Chemistry Laboratory, University of Patras, 265 00 Patras, Greece

Abstract

Laboratory kinetic experiments involving air pollutants can be performed under conditions of concentration, temperature, pressure, humidity etc., very close to those prevailing in the atmosphere, and in the presence of materials of various shapes and origin, acting as heterogeneous sinks for the pollutants. The following physicochemical parameters are determined simultaneously, under non-steady-state conditions: (1) The local adsorption parameter of the analyte pollutant A and its experimental isotherm on the surface of the material; (2) the desorption rate constant of A from the solid surface; (3) the rate constant of a possible first- or pseudofirst-order surface reaction of the adsorbed analyte A; (4) the apparent first-order rate constant of a chemical reaction of A with another pollutant B in the gaseous phase above the material; (5) the overall deposition velocity and reaction probability of A on the material, under the influence of the gaseous reaction and the real adsorption isotherm. The contribution of the above physicochemical parameters to the elucidation of the mechanism for deterioration of various materials in museums is significant, placing the whole phenomenon on a purely scientific basis.

Introduction

In the previous Symposium (Arvanitopoulou *et al.*¹), we pointed out that by organizing the experimental observations in a scientific manner, one transforms the protection and conservation of cultural heritage into a science. As an example of this, we presented a method based on a simple mathematical model for determining three rate constants, and from these the deposition velocities and reaction probabilities of air pollutants on the solid coating of the internal wall of a denuder tube. In addition to that, an integration method was described for determining rate constants of

bimolecular gaseous reactions, which may result in synergistic effects, accelerating, delaying or even inhibiting dangerous processes between pollutants and monuments. The experimental set-up of the method was that of RF-GC (Reversed-Flow Gas Chromatography) technique (Katsanos²), using a simple cylindrical denuder tube in place of the classical diffusion column.

The determination of the physicochemical parameters mentioned above assumed *linear* adsorption isotherms of the pollutants on the solid surfaces, which is an approximation used in such studies. However, in a more recent paper (Sotiropoulou *et al.*³) a simple determination of experimental isotherms was discovered, using exactly the same experimental arrangement as above, i.e. a diffusion denuder tube combined with the RF-GC technique. Incorporating this important development into the original mathematical model, non-linear isotherms without specifying *a priori* an isotherm equation, are automatically taken into account, leading to the determination of adsorption, desorption and surface reaction rate constants conforming to the real experimental isotherms. Given the complexity of the mechanism for the action of pollutants on monuments, and the importance in it of the adsorption step, one expects that the scientific basis for the conservation acts may have been improved.

The first results by using the new model, with an experimental set-up resembling that of a recent catalytic study (Topalova *et al.*⁴) were presented in the Environment/Climate ICÉC-96 Congress in Rome (Katsanos *et al.*³). Here, the solution of the relevant system of partial differential equations is more elaborate and the reacting systems consist of dimethyl sulfide and nitrogen dioxide acting on Penteli marble and a sample from an ancient statue of the National Archaeological Museum in Kavala. It is well known that dimethyl sulfide, emitted by oceanic phytoplankton, is the major natural source of sulfur in the troposphere.

Theoretical Analysis

This refers to a certain experimental arrangement (Topalova *et al.*⁴) and depends on the following mathematical model.

Local adsorption isotherm of the analyte A:

$$c_s^* = \frac{m_s}{a_s} \delta(y - L_2) + \frac{a_y}{a_s} k_1 \int_0^t c_y(\tau) d\tau \quad (1)$$

with the symbols above denoting:

c_s^* equilibrium adsorbed concentration of A at time t, mol/g.

m_s initially adsorbed amount of A, mol.

a_s amount of solid material per unit length of column bed, g/cm.

$\delta(y - L_2)$ Dirac's delta function for the initial condition of the bed, when the analyte is introduced as an instantaneous pulse at the point $y=L_2$, cm⁻¹.

- y length coordinate along section L_2 , cm.
- a_y cross sectional area of the void space in region y , cm^2 .
- k_1 local adsorption parameter, s^{-1} .
- c_y gaseous concentration of A as a function of time t and coordinate y along the column, mol/cm^3 .
- τ dummy variable for time.

Mass balance equation for the analyte A in the gaseous region z of the diffusion column:

$$\frac{\partial c_z}{\partial t} = D_1 \frac{\partial^2 c_z}{\partial z^2} - k_{\text{app}} c_z \quad (2)$$

the additional symbols being:

- c_z gaseous concentration of A as a function of time t and length coordinate z along the column, mol/cm^3 .
- D_1 diffusion coefficient of A into the carrier gas (air or nitrogen), cm^2/s .
- k_{app} apparent rate constant of a first-or pseudofirst-order reaction of A in the gas phase, s^{-1} .

Mass balance equation for A in region y of the diffusion column, filled with the solid under study:

$$\frac{\partial c_y}{\partial t} = D_2 \frac{\partial^2 c_y}{\partial y^2} - k_{-1} \frac{a_s}{a_y} (c_s^* - c_s) - k_{\text{app}} c_y \quad (3)$$

where

- D_2 diffusion coefficient of A into the gas phase in section y , cm^2/s .
- k_{-1} rate constant for desorption of A from the solid bulk, s^{-1} .
- c_s^* concentration of A adsorbed on the solid at time t , mol/g .

Rate of change of the adsorbed concentration:

$$\frac{\partial c_s}{\partial t} = k_{-1} (c_s^* - c_s) - k_2 c_s \quad (4)$$

where k_2 (s^{-1}) is the rate constant of a possible first-order or pseudofirst-order surface reaction of the adsorbed pollutant A.

With the initial conditions $c_y(0, y) = \frac{m}{a_y} \delta(y - L_2)$, and $c_s(0, y) = 0$, m being the amount (mol) of A introduced as a pulse at $y = L_2$, the solution of the system of differential eqns [1]-[4] leads to the function

$$H^{1/M} = gc(l', t) = \sum_{i=1}^4 A_i \exp(B_i t) \quad (5)$$

where

H height of sample peaks resulting from the flow reversal, cm.
 M response factor of the detector, dimensionless.
 g calibration factor of the detector, cm/mol cm³.
 $c(I', t)$ measured sampling concentration of A, mol/cm³.

The physicochemical parameters previously defined, $k_1, k_{-1}, k_2, k_{app}, D_1$ and D_2 are hidden under the exponential coefficients of time B_1, B_2, B_3 and B_4 on the right-hand side of eqn [5]:

$$X = \alpha_2(1 + V_1) + 2k_{app} + k_{-1} + k_2 = -(B_1 + B_2 + B_3 + B_4) \quad (6)$$

$$\begin{aligned}
 Y &= [\alpha_2(1 + V_1) + 2k_{app}](k_{-1} + k_2) + \alpha_1\alpha_2 + k_1k_{-1} + k_{app}^2 \\
 &\quad + \alpha_2(1 + V_1)k_{app} = B_1B_2 + B_1B_3 + B_1B_4 + B_2B_3 \\
 &\quad + B_2B_4 + B_3B_4 \quad (7)
 \end{aligned}$$

$$\begin{aligned}
 Z &= \alpha_1\alpha_2(k_{-1} + k_2) + \alpha_2V_1k_1k_{-1} + k_1k_{-1}k_2 \\
 &\quad + \alpha_2(1 + V_1)(k_{-1} + k_2)k_{app} + k_1k_{-1}k_{app} + k_{app}^2(k_{-1} + k_2) \\
 &= -(B_1B_2B_3 + B_1B_2B_4 + B_1B_3B_4 + B_2B_3B_4) \quad (8)
 \end{aligned}$$

$$W = (\alpha_2V_1 + k_{app})k_1k_{-1}k_2 = B_1B_2B_3B_4 \quad (9)$$

The symbols X, Y, Z and W are auxiliary parameters, whilst α_1, α_2 and V_1 are given by the relations

$$\alpha_1 = \frac{2D_1}{L_1^2}, \quad \alpha_2 = \frac{2D_2}{L_2^2} \quad (10)$$

$$V_1 = \frac{2V'_G(\text{empty})\epsilon}{V_G} + \frac{\alpha_1}{\alpha_2}$$

L_1 and L_2 being the lengths of the sections z and y of the diffusion column, respectively, V_G and V'_G their gaseous volumes, and ϵ the external porosity of the solid bed.

A steady-state assumption for c_i in eqn[4] leads to the same eqn[5] with $i=5$ to 7. Instead of eqns [6]-[9], the following relations are valid:

$$X_1 = \alpha_2(1 + V_1) + 2k_{app} = -(B_5 + B_6 + B_7) \quad (11)$$

$$\begin{aligned}
 Y_1 &= \alpha_1\alpha_2 + \frac{k_1k_{-1}k_2}{k_{-1} + k_2} + \alpha_2(1 + V_1)k_{app} + k_{app}^2 \\
 &= B_5B_6 + B_5B_7 + B_6B_7 \quad (12)
 \end{aligned}$$

$$Z_1 = \frac{(\alpha_2 V_1 + k_{app})k_1 k_{-1} k_2}{k_{-1} + k_2} = -(B_5 B_6 B_7) \quad (13)$$

Calculations

Using non-linear regression analysis PC programmes, one can calculate the exponential coefficients of time $B_1, B_2, B_3, B_4, B_5, B_6$ and B_7 , and from them the auxiliary parameters X, Y, Z, W, X_1, Y_1 and Z_1 . Through these, with the help of eqns[6]-[13], $k_1, k_{-1}, k_2, k_{app}$, and α_1 are computed. The α_2 value is calculated in another experiment, using only A in the absence of a second pollutant B, when $k_{app}=0$ in all eqns [6]-[13]. Finally, the overall deposition velocity V_d (cm/s) and the reaction probability γ of the analyte pollutant A on the solid material under study are found by the relations

$$V_d = \frac{k_1 V'_G(\text{empty})\epsilon}{A_s} \cdot \frac{k_2}{k_{-1} + k_2} \quad (14)$$

$$\frac{1}{\gamma} = \left(\frac{R_g T}{2\pi M_B} \right)^{1/2} \cdot \frac{1}{V_d} + \frac{1}{2} \quad (15)$$

where:

- A_s total surface area of solid, cm².
- R_g ideal gas constant, J K⁻¹ mol⁻¹.
- M_B molar mass of analyte A, kg/mol.
- T absolute temperature, K.

All above calculations are effected by the same PC program mentioned at the beginning of this section, and being available from the authors.

Some Results and Discussion

These are collected in the following Table, as examples of the application of the development exposed in the Theoretical Analysis Section. They include the local adsorption parameter (k_1), the desorption rate constant (k_{-1}), the surface reaction rate constant (k_2), the deposition velocity (V_d), the reaction probability (γ), and the gaseous reaction apparent rate constant (k_{app}), for $(\text{CH}_3)_2\text{S}$ (7.9×10^{-3} mol/dm³) acting on particles of Penteli marble and particles from the statue $\Lambda.87$ of National Archaeological Museum in Kavala (Greece). The measurements were conducted at 302-304 K, in pure N₂ atmosphere and in the absense or presence of NO₂ (18×10^{-3} mol/dm³).

Solid	NO ₂	k_1 (10 ⁻³ s ⁻¹)	k_{-1} (10 ⁻³ s ⁻¹)	k_2 (10 ⁻⁴ s ⁻¹)	V_d (10 ⁻⁹ cm/s)	γ (10 ⁻¹²)	k_{app} (10 ⁻³ s ⁻¹)
Marble ^a	No	1.09	3.72	5.40	8.30	1.03	-
Marble ^b	Yes	6.51	10.7	72.0	158	19.6	2.32
Statue ^b	No	17.1	0.178	3.43	676	84.0	-
Statue ^a	Yes	2.45	12.3	2.49	3.04	0.379	2.05

^a T=302.2 K, ^bT=304.2 K.

The theory and methodology described refers to the mechanism of damage caused by indoor environment on monumental cultural heritage, kept inside museums, churches, etc. This mechanism can be inferred in principle from the physicochemical parameters k_1 , k_{-1} , k_2 , V_d , γ and k_{app} , exemplified by their values in the above table. For example, one sees that the presence of nitrogen dioxide in a concentration double than that of methyl sulfide has an opposite effect on the above parameters in pure new marble and in pieces from an old museum statue. This is obviously due to the nature of surface of the statue drastically modified by the long time exposure to the outdoor and/or indoor environment. Another point worth observing is that the action of nitrogen dioxide comes from two directions, either through a gaseous phase homogeneous reaction with methyl sulfide (synergistic effect) or by a direct action on the solid.

It is well known that the mechanism of action of air pollutants on buildings, monuments and other cultural heritage objects consists of four basic steps in series:

- (a) Mass transfer of the gaseous pollutants to the gross exterior surface of the art piece.
- (b) Diffusional and flow transfer of the pollutants in and out of the pore structure of the object.
- (c) Activated adsorption of the gases at the interface.
- (d) Surface chemical reaction of the adsorbed pollutants, leading to the final damage of the art piece.

Stages (a) and (b) are quantitatively described by the parameters k_{-1} , V_d and k_{app} . In stage (c) k_1 is the relative parameter, while in (d) k_2 and γ are involved. All parameters are interconnected by a general damage function.

Conclusion

The mathematical model described by eqns [1]-[4], its solution leading to the master equation [5] and the scientific content of the exponential coefficients of time disclosed by eqns [6]-[13], permit the determination of the basic physicochemical parameters k_1 , k_{-1} , k_2 , V_d , γ and k_{app} by performing simple measurements with a common experimental set-up on small pieces obtained from the monuments under study. The values of these parameters can lead to the mechanism of action of air pollutants on

cultural heritage objects and the correct damage function of the phenomenon. Thus, they place the actions to be taken by conservators and museum curators on a purely scientific basis, and not on empiricism, as done so far. Naturally, an implementation stage is needed to exploit results like those in the Table for conservation purposes.

References

1. E. Arvanitopoulou, V. Sotiropoulou, N. A. Katsanos, H. Metaxa and F. Roubani-Kalantzopoulou: Measurement of Rate Coefficients Pertaining to the Mechanism of Action of Air Pollutants on Monuments, V. Fassina, H. Ott, F. Zezza (Eds.), *III Intern. Symp. Conservation of Monuments in the Mediterranean Basin*, Venice, June 1994, pp. 195-202.
2. N. A. Katsanos, *Flow Perturbation Gas Chromatography*, Marcel Dekker, New York, 1988, pp. 87-111.
3. V. Sotiropoulou, G. P. Vassilev, N. A. Katsanos, H. Metaxa and F. Roubani-Kalantzopoulou: Simple Determination of Experimental Isotherms by Diffusion Denuder Tubes, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 485-492.
4. I. Topalova, A. Niotis, N. A. Katsanos and V. Sotiropoulou: Ring Opening of Cyclohexane over ZSM-Zeolites studied by Reversed-Flow Gas Chromatography, *Chromatographia*, 1995, **41**, 227-235.
5. N. A. Katsanos, V. Sotiropoulou, F. Roubani-Kalantzopoulou and A. Kalantzopoulos: Chemical Synergistic Effects of Air Pollutants, Acting on Solid Surfaces, *Proc. Intern. Congress on Environment/Climate ICEC-96*, Rome-Italy, March 1996, In press.