INTERMITTENT DIFFUSION IN THE MODIFIED STEFAN CELL

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Abstract— A modification of the Stefan cell apparatus for the measurements of gaseous diffusion coefficients based on a continuous weighting of the amount of the evaporated solvent throughout an assembly of a capillary tubes has been developed and tested. The main result of the upgraded setup is the substantial shortening of the time interval required for obtaining reliable data needed for diffusion coefficient calculation. Details and particulars of the diffusion process in the setup are presented and discussed. Hereafter the modified Stefan cell has been used for experimental study of unsteady diffusion in case of evaporation of acetone. The relevant numerical model of the specified transient process has been implemented and used for the explanation of the experimental results.

Keywords— Stefan Cell, Solvent Evaporation, Unsteady Diffusion, COMSOL Multiphysics, Numerical Modelling.

I. INTRODUCTION

Stefan diffusion tube or the Stefan cell [1] as a simple device has been thoroughly employed for accurate measurements of gaseous diffusion coefficients in stagnant air or for the testing of the workability of Fick's or Maxwell-Stefan equations in binary or multi-component mass transfer [2-4]. However, as described in literature experimental determination of solvent diffusivities using the Stefan flow [2,3] required rather a long time for the measurements, for example, the average duration of each run in experiments with the n-pentane-air and methanol-air systems was approximately 40 hours [3]. The long time for measurements is explained by necessity to obtain a noticeable difference of the level of evaporating solvent in a single Stefan cell. The advent of precision electronic balances allows more accurate measurement of the amount of evaporated solvent by weighting in comparison with measurements by volume which reduces the time expenses [4]. Besides, some complementary capabilities of the Stefan cell can be employed. In particular, this study extends the application of the Stefan cell for the case of unsteady diffusion.

II. DETAILS EXPERIMENTAL

The principle schematic of the set-up is shown in Fig.1. Basically it consists of the set of plastic tubes assembled as a honeycomb 3 into a cylindrical glass beaker 1 which is positioned on the weighting plate of the electronic balance 5.

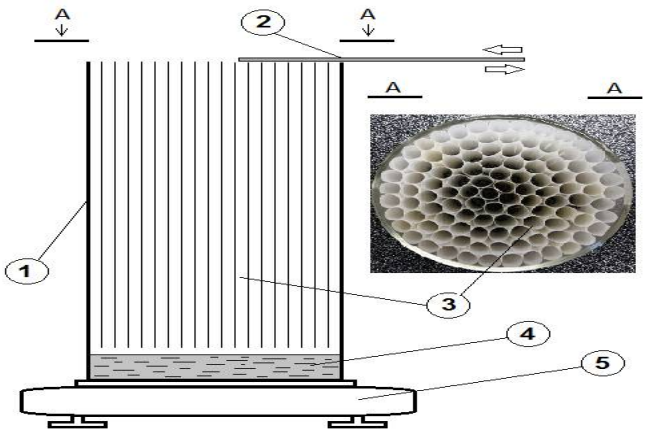


Fig.1. Schematic of experimental unit. 1 – glass beaker, 2 – movable lid, 3 – honeycomb (multi-tubes assembly), 4 – solvent, 5 – digital balance.

Commercial polypropylene cocktail straws of 6 mm diameter have been employed to form a honeycomb structure. In the bottom of the beaker is a pool of quiescent liquid 4. The composition of the vapour at the vapour-liquid interface is its equilibrium value. The vapor that evaporates from this pool diffuses through the honeycomb to the top of the unit. A draft stream of air across the top of the tubes keeps the mole fraction of the diffusing solvent vapour there to essentially zero. The application of honeycomb structure can be considered as a simultaneous use of about one hundred of single Stefan tubes. It benefits in ensuring 1-D diffusion process and fixing the path of diffusion due to insignificant change of the level of liquid when it comes to change in the mass of the order of 1 gram or less during the experiment.

Besides, in many practical applications, for example, in assessments of air pollution cases, surrounding temperature and pressure can be assumed constant within typical time interval required for data collection (~15 min.).

When the coefficient of diffusion is provided, the selected experiments were carried out to assess the capacity of the setup to operate under transient diffusion or diffusion with a periodic change of boundary conditions. A light cardboard lid 2 serves to set the open/close boundary condition at the top of the set-up.

Acetone, ethanol, and water have been tested as solvents to build up their vapour diffusion in air. The balance KERN^{TM} with minimum grade value of 0.001 g has been employed in our experiments.

It is worth pointing out the necessity of ensuring some gap between the level of liquid and the lower edge of the honeycomb, otherwise a strong capillary effect manifests itself through raising the level of the liquid in the narrow spaces between the polyethylene tubes; this results in a substantial enhancing of the evaporation rate from the setup when comparing with the standard tube of the same length. The clear evidence of rising of liquid in the narrows of the honeycomb structure (when liquid contacts with the honeycomb) has been demonstrated by using the colored ethanol (Fig.2).

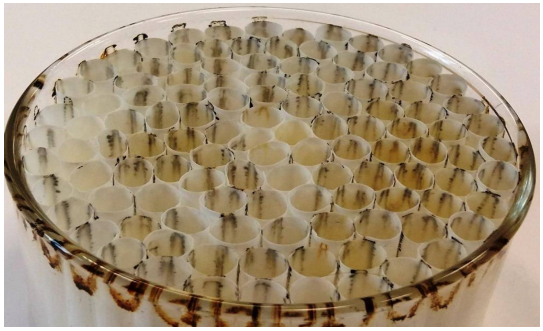


Fig.2. Evidence of capillary effect

The setup can be used also to assess tortuosity parameter for the case of diffusion throughout the fixed bed structure; in this case the honeycomb should be replaced by a cassette contained packing material.

Experiments were carried out at the ambient temperature and pressure, the typical interval for data acquisition lasted 15 - 30 min. Due to some natural variations of the ambient temperature and atmospheric pressure during experiments, it is not expected that the same precision of determining coefficient of diffusion can be achieved as in the apparatus equipped with a control and stabilization of temperature and pressure [1]. However, in many practical situations, the ambient temperature and pressure do not change significantly within half an hour; hence it is possible to determine the coefficient of apparent diffusion in the given in-situ conditions with a reasonable accuracy.

Under steady diffusion of the solvent vapour *A* throughout the stagnant air (*B*) the following solution [5] has been applied for calculation the total flux

$$j_A = \frac{cD_{AB}}{L}\ln\left(\frac{1-y_{AL}}{1-y_{A0}}\right) = \frac{P}{RT}\frac{D_{AB}}{L}\ln\left(\frac{1-y_{AL}}{1-y_{A0}}\right) \qquad (1)$$

Here the diffusion path L is assumed constant due to the negligible impact of evaporation of less than 1 g of liquid.

Equation (1) can be used to determine the coefficient of diffusion D_{AB} on the base of the measured flux j_A, which is obtained as

$$j_A = \frac{1}{M_A}\frac{\text{slope of } \Delta m \text{ vs. } t}{(\text{honeycomb cross sectional area})}, \quad [j_A] = \frac{kmol}{m^2 s}$$

where the slope is found by plotting loss of mass Δm vs. time t.

Consequently, when the coefficient of diffusion is known, or determined from the reference data according [6]

$$D_{AB} = D_{AB(ref)}\frac{P_{ref}}{P}\left(\frac{T}{T_{ref}}\right)^{\frac{3}{2}}. \qquad (2)$$

The mass loss against time for the steady process can be calculated as

$$\Delta m_A = j_A \cdot M_A \cdot S \cdot t, \qquad (3)$$

As it turned out, the experimental data on diffusion of acetone vapor through stagnant air shown in Fig.3, are in a good agreement with relationships (1)-(3).

A rather unexpected outcome has been observed in the present setup (Fig.1), when the diffusion path was periodically interrupted by means of placing the lid on and removing it off at the top of the unit; first 30 secs the apparatus was opened for the solvent vapour diffusion into surrounding space, second 30 secs diffusion path was blocked. (The readings were taken when the disturbances caused by the operations with the lid were calmed down). Considering that during the experiment half of the total time the diffusion path has been blocked, one might expect that the mass loss of acetone should be approximately reduced by a factor 2, however this value has lessened slightly (Fig.3); the observed scattering in the repeatable experiments can be attributed to some uncertainty while manual operations with the lid.

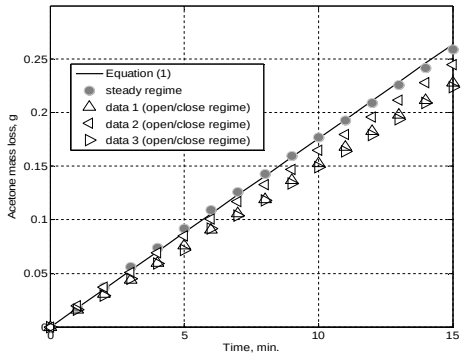


Fig. 3. Loss of mass due to diffusion of acetone vapour in the modified Stefan cell. Data obtained under the following parameters: diffusion path L = 85 mm, honeycomb cross-section area S = 0.0024 m^2; P_{atm} = 731 mm Hg, T_{amb} = 24°C.

The outcome of the experiment prompts that the expression (1) does not work in this intermittent diffusion case, hence transient effects should be counted for the case of periodic change of boundary conditions.

III. MODELING

In case of transient diffusion COMSOL Multiphysics 4.3 package has been used to obtain the numerical solution of the unsteady diffusion equation.
The physics are described by the conservation of mass species *A* (acetone) according to the following equation:

$$\frac{\partial}{\partial t}(\rho w_A)+\nabla\cdot(\rho w_A\mathbf{u})+\nabla\cdot\left[-\rho w_A D_{AB}\nabla y_A\right]=0 \qquad (4)$$

where the mixture density ρ is a function of the average mixture molar mass M_{mix}, according to equations

$$\rho=\frac{P}{RT}M_{mix} \quad M_{mix}=\sum_i y_i M_i \qquad (5)$$

The mass fraction of *B* (air) is given by

$$w_B=1-w_A \qquad (6)$$

The fact that there is no air flux at the liquid interface results in the following relation for the induced convective velocity:

$$u=\frac{n_B}{w_B\rho} \qquad (7)$$

where n_B is the diffusive mass flux of air [kg·m^{-2}s^{-1}],
Actually, two consequent transient diffusion processes has been simulated, the first corresponds to 0s < t < 30s time interval, and the second refers to 30s < t < 60 s time interval.
The model suggests that prior to the moment t = 0s, at which the lid is set on top of the Stefan cell, a steady-state diffusion takes place and, consequently, the initial profile of acetone vapour mass fraction is described by equation [5]:

$$t=0\rightarrow w_A(x)=1-(1-w_{A0})\left(\frac{1-w_{AL}}{1-w_{A0}}\right)^{\frac{x}{L}} \qquad (8)$$

with boundary conditions

$$x=0\rightarrow w_A=w_{A0},\quad x=L\rightarrow w_A=0 \qquad (9)$$

where w_{A0} is the mass fraction of vapor above the liquid interface is at equilibrium.
The temperature *T* and pressure *P* are assumed to be constant; hence the pressure build-up, which occurs in the enclosure due to change of thermodynamic equilibrium condition, has been considered as negligible for the 30 sec time interval. (This assumption is rather arguable and, perhaps, should be revised in the following for the model improvement).
The acetone vapour profile calculated at t = 30 sec (opening the lid) has been used as an initial condition for the next transient diffusion process within 30s < t < 60s with the following boundary conditions:

$$x=0\rightarrow w_A=w_{A0},\quad x=L\rightarrow w_A=0 \qquad (10)$$

In simulation the following COMSOL options have been employed:
Physics: Transport of Concentrates Species,
Diffusion Model: Maxwell-Stefan,
Space Dimension: 1D, Geometry: Interval,
Study Type: Time Dependent,
Mesh: Physics-Controlled, Extremely Fine.

IV. RESULTS AND DISCUSSION

Given the fact that the steady-mode operation of the modified Stefan cell is described satisfactory by Eqn. (8) and other known related equations [2,3,5], this discussion focuses on the interpretation of the experiment with periodic change of the boundary conditions. The evolution of profiles of acetone mass fraction for one '60 sec cycle' is shown in Fig. 4.

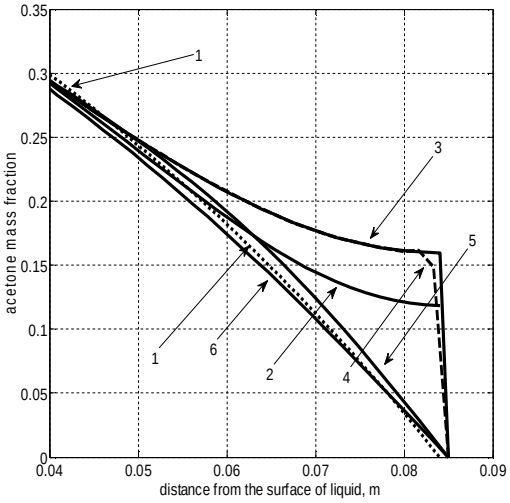


Fig. 4. Profiles of acetone mass fraction at *t* = 0s (1), *t* = 15s (2), *t* = 30s (3), (4) - a smoothening approximation of the distribution 3, *t* = 45s (5), *t* = 60s (6); curve 1 – is a steady-state profile given by Eqn. (2).

Closing the setup causes a rise of acetone mass fraction along the path between the surface of the liquid and the lid, which results in substantial increase of acetone concentration gradient at the top of the device. An accumulated acetone vapour generates a high value of the acetone mass flux at the instant after removing the lid (t = 30s), Fig. 5. In the following the profiles of acetone vapour mass fraction tend to recover the steady-state case distribution and, consequently, the value of acetone mass flux goes down. By the time t = 60s the calculated acetone mass fraction distribution nearly fits the steady-state case profile, therefore it is assumed that recovery of the original situation (t = 0) has been completed and the cycle is over.
Averaging procedure over the acetone mass flux was invoked to account for the observed (Fig. 3) nearby mass loss in the Stefan cell for the steady and intermittent diffusion of acetone vapour into the surrounding.

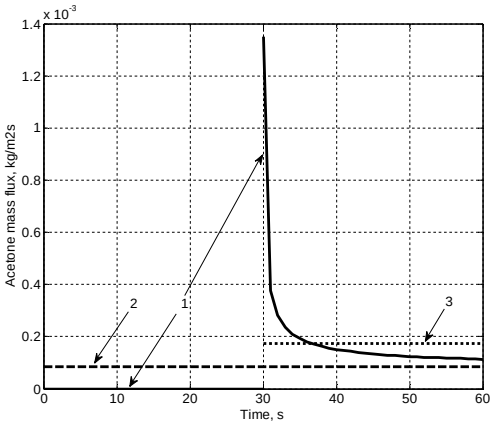


Fig. 5. Calculated acetone vapour flux at x = 0.085m. 1 – unsteady case, 2 - steady case, 3 – average value of the flux 1 within 30s < t < 60s interval.

From Fig. 5 it follows that average acetone mass flux value within 30s < t < 60s time interval for the transient case is approximately twice (line 3) the value of the flux in the stationary case (line 2); this explains the result presented in Fig. 3, i.e. inappreciable reduction of total amount of the evaporated solvent vapour for interrupted diffusion case despite the fact that during the experiment half of the total time the Stefan cell was closed.

CONCLUSIONS

1. Application of multi-tubes assembly instead of a single Stefan capillary tube allows monitoring the change of the liquid level in the capillary to be replaced with the measurement of total mass loss of evaporated solvent. As described above, the modification substantially reduces the timing interval for data acquisition.

2. Intermittent diffusion process has been carried out in the modified Stefan cell; the appropriate numerical simulation has been developed for accounting for the unsteady diffusion process. The model yields satisfactory explanation of the experimental results.

NOMENCLATURE

c	concentration, kmol·m^{-3}
M	molar mass, kg·kmol^{-1}
u	velocity, m·s^{-1}
t	time, s or min
w_A	mass fraction of A (acetone), dimensionless
w_A	mass fraction of B (air)
x	distance from liquid-vapour interface, m
y_A	mole fraction of A (acetone)

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