

KINETIC STEADY STATES IN KNUDSEN EFFUSION CELLS

M. Heyrman, C. Chatillon

Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, (UMR 5614, CNRS-INPG/UJF) – ENSEEG, Domaine Universitaire BP.75, Saint Martin d'Hères F-38402, France

Knudsen effusion cells are generally used to determine equilibrium pressures. Motzfeld¹ showed in 1955 that a Knudsen effusion cell could work with non equilibrium conditions when the rate of evaporation becomes smaller than the effusion one. From a description (fig. 1) of the different steady-state flows which are occurring in an effusion cell, and from the measured difference between the equilibrium and the real flows, he deduced the so-called "net evaporation coefficient".

Few years later, Chatillon et al.² have proposed a new description of the system by introducing gross coefficients of evaporation and condensation³ occurring at the same surface. This new method permits determining the two different coefficients in the same experiment when using the twin or multiple Knudsen cell method⁴. Hoch et al.⁵ also proposed a method based on isotopic exchange to determine condensation coefficients. The main limitation of their method when compared with our's is that the gaseous specie must be present in the vapour phase in form of a dimer or more complex molecules.

We propose a new description (fig. 2) of the Knudsen effusion cell flows in the case of two surface samples of different material reacting by the intermediate of the gas phase. We study the various possible geometries of the cells and samples. For example, if we study the interaction between two surfaces, one of C and the other of Al₂O₃, the major species in the gas phase determined by thermodynamic calculations are Al, Al₂O and CO. The behaviour of each gaseous specie on each surface are described by evaporation and condensation coefficients; for example, the evaporation coefficient of Al is different for the Al₂O₃ surface and for the C surface. Guidelines for mass spectrometric interpretation are presented.

1. Motzfeld K., J. Phys. Chem., 59, 1955, pp. 139-147.
2. Chatillon C., Rocabois P., Bernard C., High Temp.-High Press., 31, 1999, pp. 413-432.
3. Rosenblatt G.M., In Treatise on Solid-State Chemistry VI. Surfaces, Ed. N.B. Hannay, New York, Plenum Press (1976), chap. 3, pp. 165-239.
4. Chatillon C., In High Temperature Materials Chemistry, Ed. K. Hilpert, F.W. Froben, L. Singheiser, Forschungszentrums Jülich (Germany), vol. 15, part II, pp. 403-406.
5. Hoch M., Ramakrishnan D. Vernardakis T., In Advances in mass spectrometry, vol. 6, Edited by A.R. West, 1974, pp. 571-578.

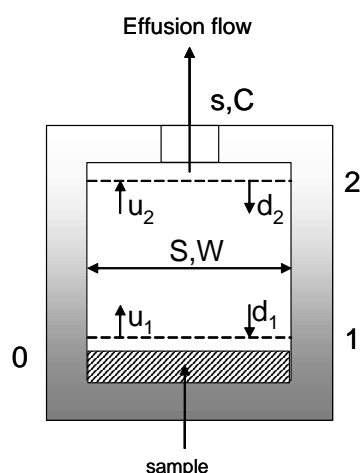


Fig. 1: Stationary state of molecular flows: s , effusion orifice cross section; C , Clausing coefficient of the orifice; S , cell cross section; W , Clausing coefficient of cell; u and d are respectively the upward and downward flows.

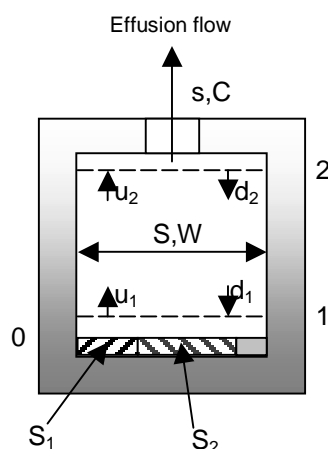


Fig. 2: Stationary state of molecular flows: s , effusion orifice cross section; C , Clausing coefficient of the orifice; S , cell cross section; W , Clausing coefficient of cell; u and d are respectively the upward and downward flows. S_1 and S_2 are the surfaces of the two different samples.