FLOW DIFFUSION CHAMBER IS A NEW TOOL FOR VAPOR NUCLEATION RATE MEASUREMENTS

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Abstract: *The quality of the vapour gas nucleation has been increased substantially in 1980th. In addition to the all known for that time experimental techniques the Flow Diffusion Chamber (FDC) was developed. Several articles devoted to FDC were published in Russian scientific journals beginning 1978 [Anisimov and co-workers (1978a,b), etc]. The scheme of FDC involves using the hot laminar vapor-gas flow within the colder boundaries which is similar, for example, to D. Sinclair and V.K. La-Mer generator of monodispersed particles. The current FDC scheme can be used for the vapor nucleation rate measurements at the total pressures from 0.3 to 3.0 Atm. FDC has been reproduced in Finland, USA, Japan, Czech Republic, Germany, Austria, and in several research groups at other countries. A conceptual problem in vapor nucleation is its treatment as a single component problem. In general, one should consider the carrier gas-vapor nucleation as a binary nucleation. In order to test the behaviour of an experimental set-up, it is useful to have a standard system that can be measured over a range of typically employed nucleation conditions. The current state of Vapor – Gas nucleation rate measurements is published recently by Anisimov et al. (2009)*

Keywords: *vapour-gas, nucleation rate measurements, flow diffusion chamber.*

1. Introduction

The flow diffusion chamber (FDC) combines advantages of the static diffusion chamber to define the nucleation conditions and simplicity of the flow systems in measuring of aerosol concentration and size distribution. FDC has decoupled aerosol generation volume and aerosol detecting zone, which is useful to grow the small critical clusters up to the optically detectable particles in the residual supersaturated vapor. FDC basic scheme is partially similar to the uniform size particle generator which is designed by Sinclair and La-Mer (1949).
Anisimov and co-workers (1978a, b) have created the original scheme of the flow diffusion chamber prototype for vapor homogeneous nucleation rate measurements. The flow diffusion chamber is developing tool up to now. FDC is reproduced in several research groups of Europe and North America at present. The strongest reason for all nucleation rate measuring system development is the data inconsistencies for the different devises. In general, one should consider the carrier gas-vapor nucleation as a binary nucleation. In order to test the behavior of an experimental set-up, it is useful to have a standard system that can be measured over a range of typically employed nucleation conditions.

2. Short Overview of the Experimental Techniques for Nucleation Studies

Presumable the first nucleation experiment was associated with measuring of the liquid and crystals supercooling which were done by Fahrenheit (Ostwald, 1896-1903). Than as Volmer mentioned in his monograph (Volmer, 1939), the gas saturated solutions, illustrated the bubble nucleation and the critical embryos of new phase, have been introduced in nucleation science at the second half of 19-th century.

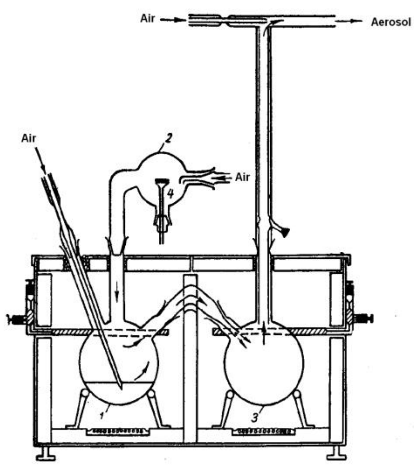

Figure 1. The generator scheme by Sinclair and La-Mer (1949) for production of monodispersed particles. Systems for vapor and heterogeneous seeds generation are numbered as (*1, 2, 4*); vapor superheater has number (*3*).

Aitken (1888) has provided practically the first research on vapor nucleation. He has used the adiabatic expansion of water vapor in air. Allen&Kassner (1969) have suggested a recompression cycle to grow the generated clusters to the optically detectable sizes. That cycle was realized later in two-piston expansion chamber (Strey *et al.*, 1986). Langsdorf (1939) has created the static diffusion chamber at the end of thirties. The Russian scientist Amelin (1948) has introduced a system where the different temperatures vapor - gas streams have been jointed in the turbulent regime.

First prototype of the Laminar Flow Diffusion Chamber was created (see, for example, Anisimov *et al.*, 1978; Anisimov&Cherevko, 1985) as an instrument for vapor homogeneous nucleation rate measurements at the end of 1970^{th}. The quality of the experimental research has been increased substantially in 1980^{-th}. The shock tube as a version of the expansion techniques got the considerable quality rise in the nucleation rate data (for example, Peters and Paikert, 1989). A shock tube represents a tube which is initially divided by diaphragm. An adiabatic expansion is initiated when the diaphragm get broken. The vapor-gas mixture from the high pressure section get vapor supersaturated under adiabatic expansion&cooling and nucleation occurs then. A shock tube (Peters&Paikert, 1989) and supersonic jets (Kim *et al.*, 2004) have the best chance for measuring the highest nucleation rate which is near 10^{11}-10^{12} $cm^{-3}s^{-1}$ now. Detailed overview of the experimental techniques, which are used for the supersaturated vapor nucleation rate measurements, is published by Anisimov *et al.* (2009). A short history of the Flow Diffusion Chamber design is presented below.

3. Flow Diffusion Chamber: Method and Results

FDC scheme involves using the hot laminar vapor-gas flow within the colder boundaries which is similar, for example, scheme of the laminar part for particle growth in the generator by Sinclair&La-Mer (1949) which is presented in Fig. 1.

3.1 Flow Diffusion Chamber scheme

Several articles devoted to FDC first versions were published by Anisimov and co-workers in scientific journals starting 1978 (Anisimov *et al.*, 1978; *etc*). A filtered carrier gas has been passing a vapor saturator, where gas was saturated. Hot vapor-gas flow entered to a cylindrical cooler/condenser. . Nucleation occurs in condenser. The present day FDC scheme is presented in Fig. 2 (Anisimov&Hopke, 2001). Gas flow laminator is used to get a fully developed laminar vapor-gas flow.

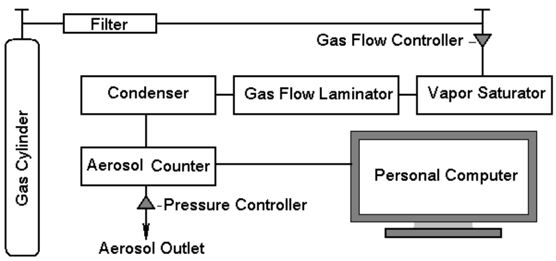

Figure 2. The present day block-scheme of the flow diffusion chamber by Anisimov at al. (2001).

That procedure makes possible to define the boundary conditions of initial vapour-gas flow velocity distribution for the stationary heat-mass transfer problemAerosol concentration and particle size distribution can be measured by aerosol counter. All experimental parameters are collected by the data acquisition unit.

The current FDC scheme is used at the total pressures from 0.03 to 0.30 MPa. Several authors (Anisimov et al., 1993; Anisimov *et al.*, 1994; Wilck *et al.*, 1998, *etc*) constructed and tested the laminar flow diffusion chamber at Helsinki University, Finland, at Clarkson University in USA (Anisimova *et al.*, 2001), Institute of Chemical Process Fundamental, Czech Republic (Brus *et al.*, 2005), *etc*.

3.2 Algorithms for the nucleation rate measurements

Algorithm for estimation of the average nucleation rates in FDC was suggested by Anisimov *et al.*, (1980). That algorithm assumes estimation of the nucleation zone and a passing time within a nucleation zone for a unit volume of a supersaturated vapor. Ratio of an experimental aerosol concentration over passing time gives the average nucleation rate. The maximum value of the nucleation rate in FDC is estimating presently using an algorithm by Wagner&Anisimov (1993). The maximum empirical value for the nucleation rate, J_{max}, in diffusion chambers can be measured using an obvious relation $J_{theor}/N_{theor}=J_{max}/N_{exp}$, where J_{theor} is maximum theoretical nucleation rate; N_{theor} and N_{exp} are the theoretical and experimental FDC particle concentrations respectively.

3.3 FDC data re-evaluation

In order to evaluate the experimental data on homogeneous nucleation rates from a laminar flow diffusion chamber experiments, a computation of the nucleation conditions is required. The influence of the used computational methodology on the derived nucleation rate curves was studied by Mitrakos *et al.* (2008).

These authors made a recalculation of published FDC experimental data for 1-butanol – helium nucleation rate measurements by Brus *et al.* (2005) using two different computational methods. The effect of total pressure on homogeneous nucleation rates of n-butanol in helium, n-pentanol in helium and argon using a laminar flow diffusion chamber were estimated by Herrmann *et al.* (2009) in a result of a computer modeling.

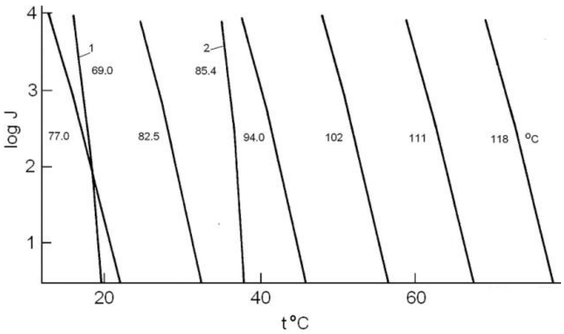

Figure 3. Experimental isobaric nucleation rate, J, of glycerin (1, 2) and dibutylphthalate on the nucleation temperature, t. Temperatures of vapor at equilibrium are presented near each curve.

3.4 FDC using Aerosol concentration was measured by nephelometer in the first experiments. Two-coordinate recorder was used to write down a variation of aerosol concentration (*y*-axis in *log*-scale) versus the saturation temperature (*x*-axis) for case of isothermal nucleation and an aerosol concentration against a cooler wall temperature for isobaric nucleation (Fig. 3). Enthalpy or/and entropy of critical embryo formation can be extracted using these kind of experimental data (Anisimov&Cherevko, 1985). Brock and co-authors designed and described a laminar coaxial flow system to study the single (Brock *et al.*,1986)) and multicomponent vapor nucleation (Brock *et al.*, 1988). These authors compared the experimentally obtained aerosol concentrations with Classical Nucleation Theory predictions and theoretical results by Wilemski (1975) for binary nucleation. It can be mentioned that for that time only four groups [Anisimov *et al.*, 1987; Brock *et al.*, 1988; Strey&Wagner, 1988 (expansion Chamber); Okuyama *et al.*, 1988 (turbulent flow)] measured the isothermal nucleation rates for two-vapors in a gas media systems within four or more orders of magnitude. Other researchers measured critical vapor supersaturations or nucleation rate within two orders of magnitude only. Nguen *et al.* (1987) was studied homogeneous and heterogeneous nucleation of a single vapor using a laminar flow aerosol generator.

3.5 Data inconsistence Results on homogeneous nucleation of n-hexanol

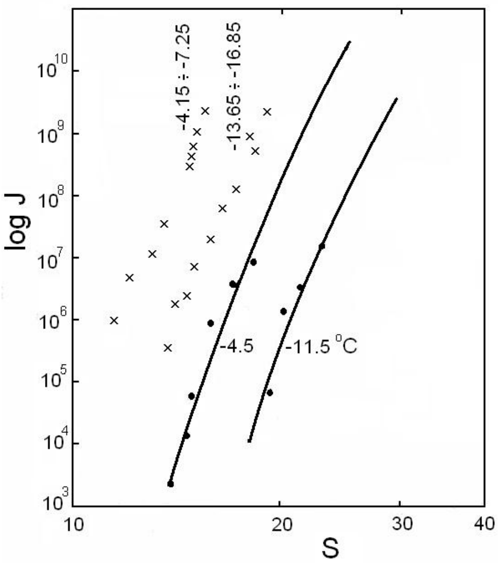

Figure 4. Comparison of the n-Hexanol experimental nucleation rate, J, versus vapor supersaturation ratio, S, from two piston expansion chamber (crosses) by Strey et al. (1986) and FDC (dots) by Anisimov – Hameri - Kulmala (1994).

(Anisimov et al., 1993; Anisimov *et al.*, 1994) were compared (Fig. 4) with data by Strey *et al.* (1986). One can see that the expansion chamber data have values on four orders of magnitude higher the FDC nucleation rate results. Slopes for the different measuring system isotherms are near the same. In the same fashion the recent data by Brus *et al.* (2005) illustrate the inconsistence the static diffusion chamber and FDC data, where the FDC values are higher the static diffusion chamber results on three and half orders of magnitude. These two examples illustrate the internal inconsistence of the experimental data, which are originated from the different experimental sets. It looks like that those experimental measurements have the uncontrollable variations of at least one physical parameter.

3.6 Empirical Gas Pressure Effect
During the past two decades several research groups provided intensive research to examine the effects of pressure and carrier gas nature on homogeneous nucleation as part of an effort to get better experimental data for probing vapor to condensed phase nucleation. Nontrivial results have appeared in using FDC. Anisimov et.al. (1998), for example, have detected experimentally the nucleation rate surface singularity which was the result of phase transition in critical embryos which are formed from both gas and vapor molecules. Articles by Anisimov, *et al.* (1998; 2000a) can be mentioned as examples, where the phase transitions in the embryo of new phase are used as markers of a gas pressure effect to show that the gas molecules are incorporated in the condensed matter.

Anisimov and Hopke (2001) have found the multichannel n-pentanol-sulfur hexafluoride nucleation. That is a case of several saddle points existence on the Gibbs free energy surface for binary system embryo formation (each of saddle point is associated with nucleation channel, see details, Anisimov and Hopke, 2001). Several results (for example, Anisimova *et al.*, 2001; Anisimov *et al.*, 1998b) are illustrating that High Pressure Flow Diffusion Chamber needs to be designed for the profound research of multichannel nucleation.

3.7 Nucleation Rate Surface Singularity
Fig. 5 illustrates the example of the experimental data where the gap in nucleation rate can be seen. Gap is initiated by the phase change in critical embryos which are generated from supersaturated vapor-gas system (Anisimov *et al.*, 1998). A conceptual problem in vapor - liquid nucleation is its treatment as a single component problem. In general, one should consider the carrier gas-vapor nucleation as a binary system, such as it was proved by Anisimov *et al.* (1998, 2000a, b). Another aspect of nucleation experiments is appeared when the probability of phase change in the critical embryo exists. Phase change means the statistical prevail of other phase state embryos generation over the initially prevailing embryo phase state. That result was obtained on the example of glycerine vapour nucleation and condensation (Anisimova *et al.*, 2001). These authors have found bimodal aerosol particle size distribution which was initiated by two different embryo phase states.

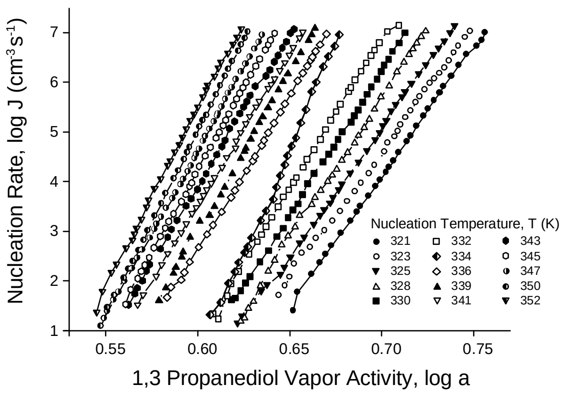

Figure 5. Nucleation rates for 1,3 Propanediol – Sulphur Hexafluoride System at total pressure 0.3 MPa. The gap in nucleation rate is associated with phase state change in the condensate critical embryos of binary system (Anisimov et al., 2000a)

Anisimova *et al.* (2001) examined nucleation in the vicinity of the glycerine triple point using FDC and applied the particle size measurements to observe two condensed phases which are generated via two independent nucleation channels, representing two nucleation rate surfaces. The experimental scheme by Anisimova *et* *al.* (2001) with the size distribution measurements can be an effective tool for independent measurements of nucleation rates for each nucleation channel. A major problem in detection of the nucleation rate surface singularities is the random errors inherent in any experimental data (Fig. 5). This problem exists even one has experimental results of high accuracy such as those of Strey *et al.* (1995), where a nucleation rate surface singularity was missed. Anisimov *et al.* (2000c) suggested using the mathematical condition of the continuity and monotony for FDC data analysis to find the anomalies of the nucleation rate surfaces.

4. Conclusions

Flow diffusion chamber as an instrument for vapor homogeneous nucleation rate measurements was appeared at the end of 1970th. The flow diffusion chamber is presenting the world wide distributed tool for the vapor nucleation rate measurements at low and elevated pressure conditions from 0.03 MPa to 0.4 MPa and nucleation temperatures from -30 to 80 ^{o}C currently. FDC is permanently developing system, which can be used for single as well as multi-component vapor–gas nucleation under the relatively wide variation of nucleation conditions. FDC can be developed easily for measurements at pressures up to 20 MPa. Several results (for example, Anisimova *et al.*, 2001; Anisimov *et al.*, 1998) are illustrating that High Pressure Flow Diffusion Chamber needs to be designed for the profound research of multi-channel nucleation. The introduction of one or several nucleation standard(s) is an actual current problem. The dipper understanding of the carrier-gas effects will clarify the nature of the different experimental set data inconsistencies (Anisimov *et al.*, 2009). FDC is capable tool for the vapor nucleation rate measurements as well as other tools such as the expansion & jet techniques and the static cloud chambers.

5. References

Aitken, J., (1888) *Trans. Roy. Soc. Edinburgh*, **35**, 1.

Allen, L.B. and Kassner, J.L., Jr. (1969) *J. Colloid Interface Sci.* **30**, 81- 93.

Amelin, A.G. (1948) *Colloidn. Zh.* (Russian), **10**, 169-176.

Anisimova, L., Hohke, P.K., and Terry, J. (2001) *J. Chem. Phys.*, **114**, 9852-9855.

Anisimov, M.P., Costrovskii, V.G., and Shtein, M.S. (1978a) *Colloidn. Zh.* (Russian) **40**(1), 116-121.

Anisimov, M.P., Costrovskii, V.G., and Shtein, M.S. (1978b) *Colloidn. Zh.* (Russian) **40**(2), 317-321.

Anisimov, M.P., Costrovskii, V.G., Shtein, M.S, and Mikheev, V.B. (1980) *Colloidn. Zh.* (Russian) **42**, 941-945.

Anisimov, M.P. and Cherevko, A.G. (1985) *J. Aerosol Sci.*, **16**(2), 97-107.

Anisimov, M. P., Hameri, K., Kulmala, M., Ovchinnikova, T.E. (1993) *Report Series in Aerosol Sci.*, **23**., 19-24.

Anisimov, M.P., Hameri, K., Kulmala, M. (1994) *J. Aerosol Sci.*, **25**(1), 23-32.

Anisimov, M.P., Koropchak, J.A., Nasibulin, A.G., and Timoshina, L.V. (1998) *J. Chem. Phys.*, **109**(22): P. 10004-10010

Anisimov, M.P., Koropchak, J.A., Nasibulin, A.G., and Timoshina, L.V. (2000a) *J. Chem. Phys.*, **112**(22), 9917-9928.

Anisimov, M.P.; Nasibulin, A.G., Shandakov, S.D., (2000b) *J. Chem. Phys.* **112**(5), 2348-2354.

Anisimov, M.P.; Nasibulin, A.G., Shandakov, S.D., (2000c). *J. Chem. Phys.* **112**(5) 2348 - 2354

Anisimov, M.P. and Hopke, P.K. (2001) *J. Phys. Chem. B*. **105**, 11817-11822

Anisimov, M.P., Fominykh, E.G., Akimov, S.V., Hopke, P.K. (2009) *J. Aerosol Sci.* **40**, 733-746

Brock, J.R., Kuhn, P.J. and Zenavi, D. (1986). *J. Aerosol Sci.*, **17**, 11-22.

Brock, J.R., Kuhn, P.J. and Zenavi, D. (1988). *J. Aerosol Sci.*, **19**, 413-424.

Brus, D., Hyvarinen, A.. Zdimal, V. and Lihavainen H. (2005) *J. Chem. Phys.*, **122**, 214506.

Herrmann, E., Hyvärinen, A.P., Brus, D., Lihavainen, H., Kulmala, M. (2009) *J Phys Chem A*. Feb 3. [E-pub ahead of print]

Kim, Y.J., Wislouzil, B.E., Wilemski, G., Wolk, J., and Strey, R. (2004). *J. Phys. Chem. A* **108**, 4365-4377

Langsdorf, A. (1939) *Rev. Sci. Instr*. **10**, 91-103.

Mitrakos, D., Zdímal, V., Brus, D., Housiadas, C. (2008). *J Chem Phys.* Aug 7, **129**(5), 054503.

Nguyen, H. V., Okuyama, K., Mimura, T., Kousaka, Y., Flagan, R.C., and Seinfeld, J. H. (1987) *J. Colloid Interface Sci.*, **119**, (2), 491-504

Okuyama, K., Kousaka, Y., Kreidenweis, S., Flagan, R.C., and Seinfeld, J.H. (1988). *J. Chem. Phys*., **89**(10), 6442-6453.

Ostwald, W. (1896-1903) *Lehrbuch der Allgemeinen Chemie*. Leipzig, W.Engelmann.

Peters F. and Paikert B. (1989) *J. Chem. Phys*. **91**, 5672-5678.

Strey, R. and Wagner, P.E., Schmeling, T. (1986) *J. Chem. Phys.* **84**(4), 2325 - 2335;

Strey, R. and Wagner, P.E. (1988) *J. Aerosol Sci.*, **19**, 813-816.

Strey, R.; Viisanen, Y.; Wagner, P.E. (1995) *J. Chem. Phys.* **103**(10), 4333-4345.

Sinclair, D. and La-Mer V.K. (1949) *Chem Rev*. **44**, 245-251

Volmer, M. (1939) *Kinetik der Phasenbildung.* Dresden-Leipzig, T. Steinkopf

Wagner, P.E. and Anisimov, M.P. (1993) *J. Aerosol Sci*., **24**, Suppl.1., 103-104.

Wilck, M., Hameri, K., Stratmann, F., and Kulmala, M. (1998) J.Aerosol Sci. 29(8), 899-911.

Wilemski, G. (1975), *J. Chem. Phys.*, **62**, 3763-3771.