Aerosol Science and Technology: History and Reviews

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About the Cover

The cover depicts an important episode in aerosol history—the Pasadena experiment and ACHEX. It includes a photograph of three of the key organizers and an illustration of a major concept of atmospheric aerosol particle size distribution. The photograph is from Chapter 8, Figure 1. The front row shows Kenneth Whitby, George Hidy, Sheldon Friedlander, and Peter Mueller; the back row shows Dale Lundgren and Josef Pich. The background figure is from Chapter 9, Figure 13, illustrating the trimodal atmospheric aerosol volume size distribution. This concept has been the basis of atmospheric aerosol research and regulation since the late 1970s.

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CHAPTER 17

History of the Flow Diffusion Chamber Development

Michael Anisimov

Introduction

The flow diffusion chamber (FDC) combines the ability of a static diffusion chamber to define the nucleation conditions with the simplicity of flow systems for measuring aerosol concentration and size distribution. It decouples aerosol generation volume and aerosol detecting zones, which is useful for growing small critical clusters into optically detectable particles in residual supersaturated vapor. The FDC's basic scheme is similar to that of the uniform size particle generator designed by Sinclair and La-Mer (1949). Anisimov and colleagues (1978a, 1978b) created the original FDC prototype for vapor-homogeneous nucleation rate measurements. The FDC has continued to develop since that time, and several research groups in Europe and North America have reproduced the FDC. The strongest reason for developing similar systems to measure nucleation rates is that data inconsistencies are observed between different devices.

Short Overview of the Experimental Techniques for Nucleation Studies

Presumably, the first nucleation experiments were associated with the liquid and crystal supercooling measurements that Daniel Gabriel Fahrenheit conducted (Ostwald, 1896–1903). Then, as Volmer (1939) notes, in the second half of the nineteenth century, nucleation science introduced gas-saturated solutions, characterized by bubble nucleation and the critical embryos of the new phase formation. Aitken (1888) provided the first research on vapor nucleation. He used adiabatic expansion of water vapor in air. Allen and Kassner (1969) suggested a recompression cycle to grow the generated clusters to optically detectable sizes. The two-piston expansion chamber later realized this cycle (Strey et al., 1986). At the end of the 1930s, Langsdorf (1939) created the static diffusion chamber. It consisted of two wet plates under different

temperatures. The vapor diffusion and temperature gradient provided the vapor supersaturation, thereby causing nucleation to occur under appropriate conditions. The Russian scientist Amelin (1948) introduced a system in which vapor-gas streams with different temperatures were joined in the turbulent regime.

At the end of the 1980s, Anisimov and colleagues (see, e.g., Anisimov et al., 1978a,1978b; Anisimov & Cherevko, 1985) created the first prototype of the laminar flow diffusion chamber (LFDC) as an instrument for measuring vapor homogeneous nucleation rates. The quality of experimental research increased substantially in the 1980s. Peters & Paikert (1989) developed the shock tube as an expansion technique that allowed the high-quality nucleation rate measurements. A shock tube is a tube containing a diaphragm that initially forms two chambers, one of which has a higher pressure than the other. When the diaphragm ruptures, an adiabatic expansion occurs. With expansion and adiabatic cooling, the vapor-gas mixture from the high-pressure section forms a supersaturated vapor with subsequent nucleation. A shock tube (Peters & Paikert, 1989) and supersonic jets (Kim et al., 2004) have demonstrated the highest measured nucleation rates, in the range of 10^{11} to 10^{12} $cm^{-3}s^{-1}$. Unfortunately, agreement between experimentally measured vapor nucleation rates and current theoretical predictions exists only for a limited number of systems. Anisimov and colleagues (2009) provide a detailed review of the experimental techniques used for supersaturated vapor nucleation rate measurements. This chapter presents a short history of the FDC design.

Flow Diffusion Chamber: Method and Results

The FDC scheme involves using hot laminar vapor-gas flowing within colder boundaries. The chamber is similar to, for example, the laminar part of the apparatus for particle growth in the aerosol generator developed by Sinclair and La-Mer (1949), which Figure 1 presents. The laminar vapor-gas flows out of the vapor superheater (Figure 1) to grow heterogeneous seeds that can obtain uniform-size particles.

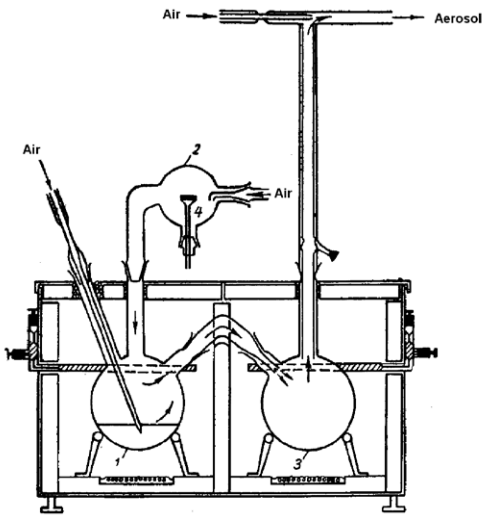

Figure 1. Sinclair and La-Mer's (1949) generator scheme for producing monodispersed particles. Systems for vapor and heterogeneous seeds generation are numbered as 1, 2, and 4; the vapor superheater is number 3.

Flow Diffusion Chamber Scheme

Several articles devoted to the first versions of the FDC were published by Anisimov and colleagues in scientific journals (e.g., Anisimov et al., 1978a, 1978b). Figure 2 shows one of the first versions of the aerosol generator (Anisimov & Cherevko, 1985). This aerosol generator is an open system that operates under atmospheric pressure. Gas pressure from a high-pressure cylinder is reduced to appropriate pressure conditions. A filtered carrier gas passes through a vapor saturator, in which the substance under investigation saturates the gas. The hot vapor-gas flow then enters a cylindrical cooler. Coaxial cooled gas surrounds the hot vapor-gas in the cooler/condenser. The laminar vapor-gas flow then becomes supersaturated, and nucleation occurs in the condenser.

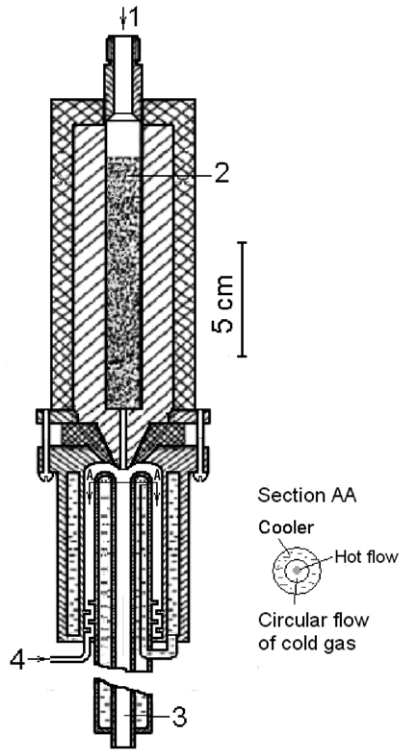

Figure 2. This scheme shows the first version of Anisimov and colleagues' (1978a) aerosol generator. The filtered carrier gas is 1; the vapor saturator is 2; the cooler/condenser is 3; the axial rung-shape co-flow system for cooled gas is 4. A laminar vapor-gas flow becomes supersaturated, and nucleation occurs in the condenser.

Figure 3 shows the current FDC scheme (Anisimov & Hopke, 2001). A filtered carrier gas passes through a flow controller and, in the saturator, becomes saturated with the substance under investigation. The FDC uses a flow laminator to obtain a fully developed laminar vapor-gas flow. That procedure makes it possible to define the boundary conditions of the initial vapor-gas flow velocity distribution for input to the stationary heat-mass transfer problem. Nucleation occurs in the condenser. An aerosol counter measures aerosol concentration and particle size distribution; the counter is placed in front of the pressure controller to avoid the nucleation artifacts in the controller caused by pressure drop. The data acquisition unit collects all experimental parameters. The current FDC measures vapor nucleation rates at total pressures of 0.03 to 0.30 MPa. Several research teams (e.g., Anisimov et al., 1993, 1994; Wilck et al., 1998) have constructed and tested the LFDC at Helsinki University, Finland; Clarkson University, Pottsdam, New York (Anisimova et al., 2001); the Institute of Chemical Process Fundamental, Czech Republic (Brus et al., 2005); and other institutions.

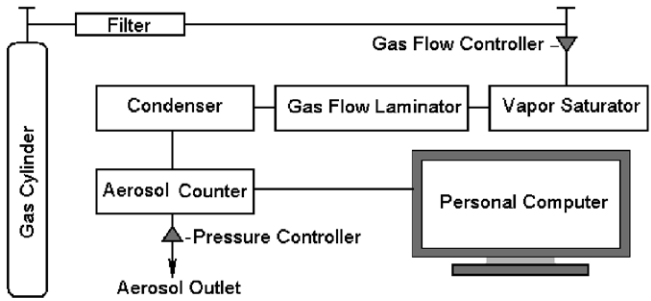

Figure 3. Anisimov and Hopke's (2001) block-scheme for the flow diffusion chamber; still in current use.

Algorithms for the Nucleation Rate Measurements

Anisimov and colleagues (1980) suggest an algorithm for estimating the average nucleation rates in FDC. That algorithm assumes an estimation of the nucleation zone and a residence time within a nucleation zone for a unit volume of a supersaturated vapor. The ratio of experimental aerosol concentration over the aerosol residence time gives the average nucleation rate. The maximum value of the nucleation rate in the FDC is currently estimated using an algorithm described by Wagner and Anisimov (1993).

One can measure the maximum empirical value of nucleation rate, J_{max}, in diffusion chambers using an obvious relationship $J_{theor} / N_{theor} = J_{max} / N_{exp}$, where J_{theor} is maximum theoretical nucleation rate; N_{theor} and N_{exp} are the theoretical and experimental FDC particle concentrations, respectively.

Flow Diffusion Chamber Data Re-evaluation

Evaluating the experimental homogeneous nucleation rates data from LFDC experiments requires a computation of the nucleation conditions. Mitrakos and colleagues (2008) studied the influence of the computational methodology used on the derived nucleation rate curves. These authors recalculated FDC experimental data published by Brus and colleagues (2005) by using two different computational methods for measuring 1-butanol–helium nucleation rates. FDC data evaluations commonly use the first method, which is based on single fluid heat and vapor transport in the carrier gas, ignoring aerosol generation. The second method is more comprehensive and is based on multidimensional computational fluid-particle dynamics. These two methods produced nearly the same results. This finding corroborates the usual approach of neglecting aerosol generation in the mass transfer problem solution when evaluating FDC experimental data.

Herrmann and colleagues (2006) used the computational fluid dynamics software FLUENT in combination with the fine particle model (FPM) for aerosol dynamics calculations to verify experimental data obtained by Hyvärinen and colleagues (2006). The calculated results for the nucleation conditions were practically identical to those computed by Hyvärinen and colleagues (2006). Herrmann and colleagues (2009) used this computer model to estimate the effect of total pressure on homogeneous nucleation rates of *n*-butanol in helium, *n*-pentanol in helium, and argon using a LFDC.

Flow Diffusion Chamber Use

Anisimov and Cherevko (1985), in the first experiments, used a nephelometer to measure aerosol concentration in the FDC. A two-coordinate recorder documented variations in aerosol concentration (y-axis in log-scale) versus the saturation temperature (x-axis). That case was presented as the isothermal nucleation rate. A nucleation temperature was varied at constant partial vapor pressure to obtain the isobaric vapor nucleation rates. Figure 4 shows the first examples of isobaric nucleation rate data. As Anisimov and Cherevko (1982, 1985) show, this type of experimental data can help to determine the enthalpy and/or entropy of critical embryo formation.

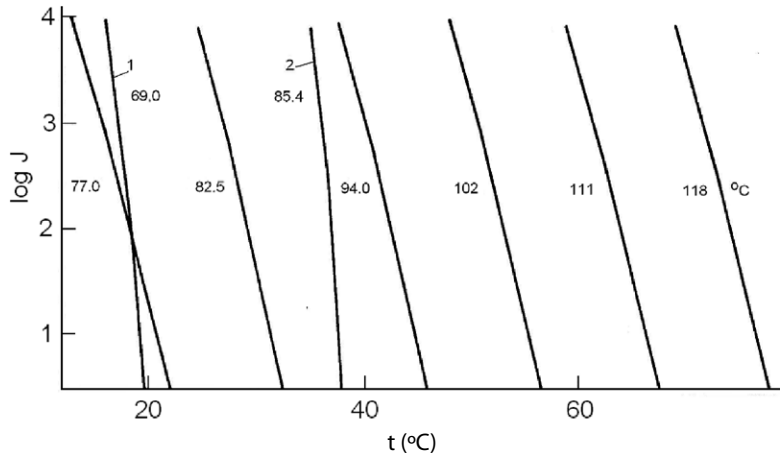

Figure 4. Experimental isobaric nucleation rate, J, of glycerin (1, 2) and dibutyl phthalate on the nucleation temperature, t. The temperatures of vapor at equilibrium are presented near each curve.

Brock and colleagues designed and described a laminar coaxial flow system to study single-component (Brock et al., 1986) and multicomponent (Brock et al., 1988) vapor nucleation. These authors compared the experimentally obtained aerosol concentrations with classical nucleation theory predictions and the theoretical results for binary nucleation that Wilemski (1975) describes. In the late 1980s, only four groups measured the isothermal nucleation rates for two vapors in gas media systems within a range of 4 or more orders of magnitude (Anisimov et al., 1987; Brock et al., 1988; Strey & Wagner, 1988 [expansion chamber]; Okuyama et al., 1988 [turbulent flow]). At that time, other researchers measured critical vapor supersaturations or nucleation rates within a range of only 2 orders of magnitude for two vapors in a gas media systems (e.g., Mirabel & Clavelin, 1978; Kulmala et al., 1988).

Nguyen and colleagues (1987) studied homogeneous and heterogeneous nucleation of a single vapor using a laminar flow aerosol generator. Kodenev and colleagues (1987) experimented with applying the Thomson equation to small clusters using FDC and the "nucleation theorem" (Kashchiev, 1982; Oxtoby & Kashchiev, 1994; see also Anisimov et al. 1978b, 1980, 1987; Anisimov & Cherevko, 1982, 1985).

Data Inconsistencies

Anisimov and colleagues (1993, 1994) compared homogeneous nucleation results of n-hexanol with data obtained by Strey and colleagues (1986) (Figure 5). The expansion chamber data are 4 orders of magnitude higher than the FDC nucleation rate results. However, slopes for the isotherms obtained with different experimental systems are nearly the same. In the same fashion, recent data obtained by Brus and colleagues (2005) illustrate the inconsistencies between the static diffusion chamber and FDC data; the FDC values are higher than the static diffusion chamber results by 3.5 orders of magnitude (Figure 6). These two examples illustrate the internal inconsistency of experimental data from different experimental sets because those experimental measurements have uncontrollable variations of at least one physical parameter.

One can better understand the nature of the data discrepancy when one recalls that Anisimov and colleagues (1998a) designed the nucleation rate surfaces. Considering vapor-gas as a binary system in terms of nucleation helps one to see how different experimental systems can obtain different

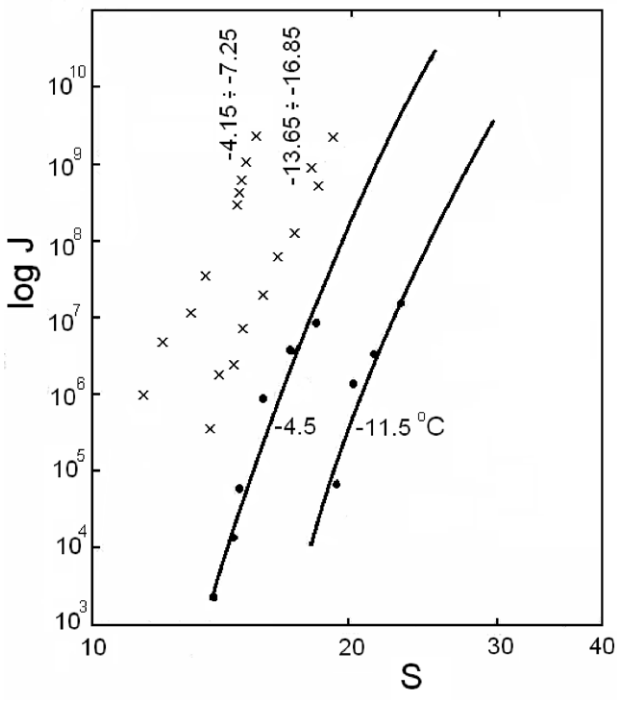

Figure 5. Comparison of the n-hexanol experimental nucleation rate, J, versus vapor supersaturation ratio, S, from the two-piston expansion chamber (crosses) by Strey and colleagues (1986) and the flow diffusion chamber (dots) by Anisimov and colleagues (1994).

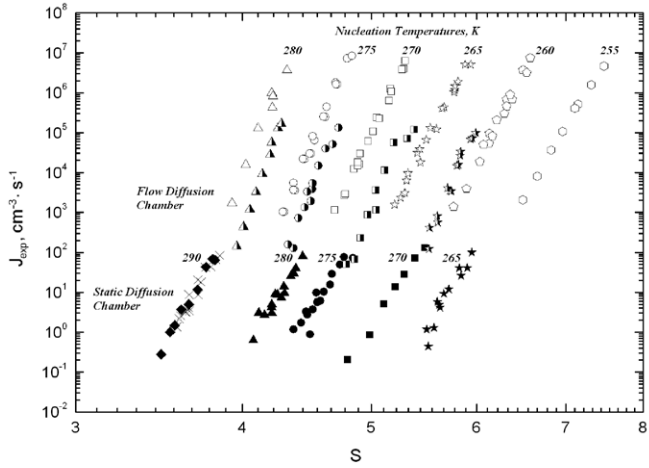

Figure 6. Recent data by Brus and colleagues (2005) illustrate the inconsistent results obtained by the static diffusion chamber and the laminar flow diffusion chamber (LFDC), which are caused by the different experimental trajectories in the space of nucleation conditions (Anisimov et al., 2009). Denotation J_{exp} indicates the experimental nucleation rates as a function of saturation ratio, S, for 1-butanol. Filled symbols: from left to right, the static diffusion chamber at temperatures of 290, 280, 275, 270, and 265 °K. Half-filled symbols: from left to right, new LFDC at temperatures of 280, 275, 270, and 265 °K. Open symbols: Lihavainen and Viisanen (1998a, 1998b) at temperatures of 280–255 °K at 5 °K intervals from left to right. Crosses: the static diffusion chamber at temperature of 290 °K and at 120 kPa pressure (Brus et al., 2005).

trajectories of the experimental conditions and associated nucleation rates on the nucleation surface. Currently, gas is treated, in most cases, as an inert medium that absorbs the heat from the phase transition; however, experimental and theoretical evidence exists that vapor-gas should be considered as a binary system. That different experimental systems have inconsistent trajectories on the nucleation rate surface, representing vapor-gas nucleation as the nucleation of a binary system, is quite plausible.

Empirical Gas Pressure Effect

During the past two decades, several research groups have performed intensive research on the effects of pressure and the type of carrier gas on homogeneous nucleation. This research is part of an effort to obtain better

experimental data for probing vapor to condensed phase nucleation. Using the FDC has produced nontrivial results. Anisimov and colleagues (1998b), for example, experimentally detected a nucleation rate surface singularity that resulted from phase transition in critical embryos formed from both gas and vapor molecules. Anisimov and colleagues (1998b; 2000a) document instances in which the phase transitions in the embryo of the new phase are used as markers of a gas-pressure effect to show that the gas molecules are incorporated into the condensed matter. Anisimov and Hopke (2001) found multichannel *n*-pentanol–sulfur hexafluoride nucleation. In that case, the Gibbs free energy surface has several saddle points for the formation of binary system embryos (each saddle point is associated with a nucleation channel; for details, see Anisimov & Hopke, 2001). Several studies (e.g., Anisimova et al., 2001; Anisimov et al., 1998b) have shown that a high-pressure flow diffusion chamber needs to be designed for the profound research of multichannel nucleation. While a new experimental system is in development, researchers have used an existing FDC to study nucleation systems. Using the FDC, researchers have shown that the carrier gas and multiphase phenomena have effects that need to be explored further.

Nucleation Rate Surface Singularity

Figure 7 provides an example of experimental data that shows the gap in nucleation rate. The gap is initiated by the phase change in critical embryos generated by a supersaturated vapor-gas system (Anisimov et al., 1998b). A conceptual problem in vapor-liquid nucleation is that it is treated as a single-component problem. In general, the carrier gas–vapor nucleation should be considered as a binary system, as Anisimov and colleagues (1998b, 2000a, 2000b) have proved.

Another possible avenue for nucleation experiments opens when a phase change in the critical embryo is probable. Phase change means that the generation of other phase state embryos statistically prevails over the initially prevailing embryo phase state. We have not yet mentioned the phase transition in the single cluster. Apparently, when critical clusters grow, the initial phase state of the critical embryo can exist for a longer time relative to the nucleation and embryo growth time interval. Anisimova and colleagues (2001) obtained that result using the example of glycerine vapor nucleation and condensation. These researchers found a bimodal aerosol particle size distribution that was initiated by two different embryo phase states. The

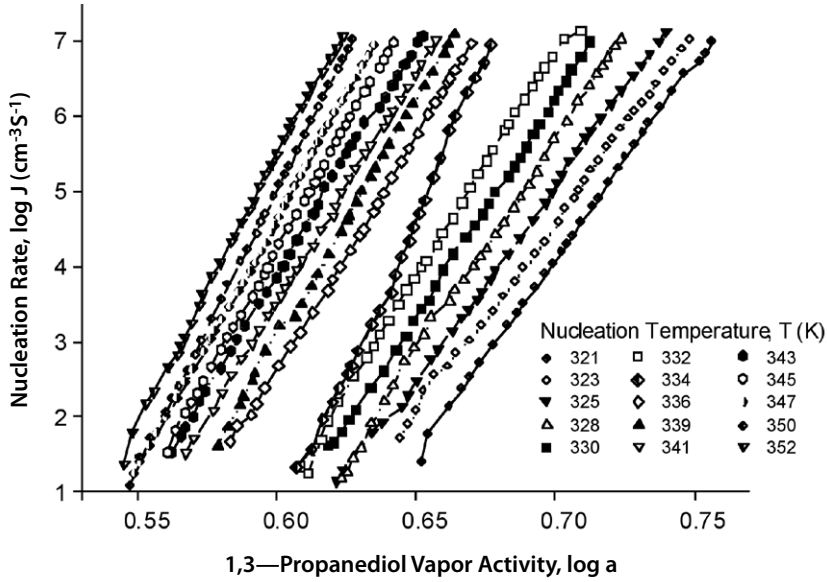

Figure 7. Nucleation rates for the 1,3–propanediol–sulphur hexafluoride system at a total pressure of 0.3 MPa. The gap in nucleation rate is associated with the phase state change in the condensate critical embryos of the binary system (Anisimov et al., 2000c).

phase transitions in the growing clusters acted to smooth the clearly detected bimodal size distribution of glycerine particles in those measurements (Anisimova et al., 2001).

The random errors inherent in any experimental data pose a major problem in detecting nucleation rate surface singularities (Figure 7). This problem exists even in highly accurate experimental results such as those produced by Strey and colleagues (1995); in that study, the results missed a nucleation rate surface singularity. Anisimov and colleagues (2000b) suggest using the mathematical condition of the continuity and monotony for FDC data analysis to find the anomalies of the nucleation rate surfaces.

Anisimova and colleagues (2001) examined nucleation in the vicinity of the glycerine triple point using FDC and applied the particle size measurements to observe two condensed phases generated by two independent nucleation channels, representing two nucleation rate surfaces. The experimental scheme that Anisimova and colleagues (2001) propose uses size distribution measurements and can be an effective tool for measuring nucleation rates independently for each nucleation channel.

Vapor Nucleation Rate Standard

In order to test the accuracy of an experimental setup, one must have a standard system that can be measured over a range of typical nucleation conditions. The Nucleation Experiments—State of the Art and Future Development workshop, held in 1995 in Prague—proposed using the *n*-pentanol–helium system for such measurements. Anisimov and colleagues (2000c) presented the results of the available experimental results from several research groups. The data were parameterized using classical nucleation theory with Tolmen's correction for surface tension. The fitting parameter, δ, was equal to 0.4 angstroms. The resulting approximation can be presented as

$$J_{fit} = \frac{V}{(kT)^2}\sqrt{\frac{2\sigma}{\pi \cdot M}} \cdot P^2 \cdot exp\left(-\frac{16\pi \cdot \sigma^3 \cdot V^2}{3(kT)^3 \cdot (lnS)^2} \cdot \left(1 - \frac{2\beta}{lnS} \cdot \frac{P_{tot} - P_{atm}}{P_{atm}}\right)\right), \quad (1)$$

where J_{fit} is vapor nucleation rate, P_{tot} is total pressure, V is the volume per molecule in the liquid phase, and S is the vapor supersaturation ratio. The equation for surface tension, σ, is applied as $\sigma = \sigma_0 / (1 + 2\delta / r^*)$, where σ_0 is the surface tension for a bulk liquid, and r^* is the radius of critical embryos. The fitting parameter, β, is expressed as $\beta = 1.486T_r^3$, where $T_r = T / T_c$ is the reduced nucleation temperature; T_c is the critical temperature of *n*-pentanol, which is equal to 588.15 K. The critical embryo radius is calculated as $r^* = 2\sigma M / (RT\rho lnS)$, where M is the molecular weight of *n*-pentanol and R is the universal gas constant. The term for the pressure effect was taken into the linear approximation as $(2\beta / lnS)(P_{tot} - P_{atm}) / P_{atm}$ for experimental data obtained by van Remoortere and colleagues (1996) and Anisimov and colleagues (2000c). Recently, Hyvärinen and colleagues (2007) have found the positive and negative pressure effects of that system.

Although one can criticize Anisimov and colleagues (2000c) for this approximation, there is currently no alternative to it. In its present form, the approximation is useful for comparing results obtained by the different research groups until a better description of the pressure effect is discovered. The problem of the nucleation standard will seemingly be solved when independent research groups can obtain consistent results with the different experimental schemes. We believe that the vapor-gas nucleation rate should be represented by a surface rather than by the single line currently used in most isothermal nucleation data for vapor-gas systems.

Conclusion

The FDC for vapor homogeneous nucleation rate measurements first appeared at the end of the 1970s. The FDC is used worldwide to measure vapor nucleation rates at low and elevated pressure conditions from 0.03 MPa to 0.4 MPa and nucleation temperatures from –30°C to 80°C. The FDC is a well-developed system, which can be used for single and multicomponent vapor-gas nucleation under a relatively wide variety of conditions. The FDC can be developed easily for measurements at pressures up to 20 MPa. Several results illustrated that a high-pressure flow diffusion chamber should be designed for the careful research of multichannel nucleation (e.g., Anisimova et al., 2001; Anisimov et al., 1998a, 1998b). While a new experimental system is being developed, research teams have used existing FDCs to study nucleation systems, showing that there are effects of the carrier gas and multiphase phenomena that need to be explored further. Experimentalists will hopefully find the uncontrollable parameter(s) soon in order to obtain consistent nucleation rate data from several research groups with different experimental schemes. Difficulty developing one or several nucleation standard(s) has been an ongoing problem. Developing a successful nucleation standard and introducing this standard into common nucleation research practice will be key advancements in the field. Having a better understanding of the effects of carrier gas will clarify the nature of the inconsistencies between different experimental data sets (Anisimov et al., 2003, 2009). The FDC is an important and capable tool for measuring vapor nucleation rates as well as expansion jet techniques and static cloud chambers.

Acknowledgments

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