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EXPERIMENTS ON HOMOGENEOUS NUCLEATION AND
PHYSICOCHEMICAL PROPERTIES RELATED TO
ATMOSPHERIC NEW PARTICLE FORMATION

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Academic dissertation

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ABSTRACT

Aerosol particles play a role in the earth ecosystem and affect human health. A significant pathway of producing aerosol particles in the atmosphere is new particle formation, where condensable vapours nucleate and these newly formed clusters grow by condensation and coagulation. However, this phenomenon is still not fully understood. This thesis brings an insight to new particle formation from an experimental point of view. Laboratory experiments were conducted both on the nucleation process and physicochemical properties related to new particle formation.

Nucleation rate measurements are used to test nucleation theories. These theories, in turn, are used to predict nucleation rates in atmospheric conditions. However, the nucleation rate measurements have proven quite difficult to conduct, as different devices can yield nucleation rates with differences of several orders of magnitude for the same substances. In this thesis, work has been done to have a greater understanding in nucleation measurements, especially those conducted in a laminar flow diffusion chamber. Systematic studies of nucleation were also made for future verification of nucleation theories.

Surface tensions and densities of substances related to atmospheric new particle formation were measured. Ternary sulphuric acid + ammonia + water is a proposed candidate to participate in atmospheric nucleation. Surface tensions of an alternative candidate to nucleate in boreal forest areas, sulphuric acid + dimethylamine + water, were also measured. Binary compounds, consisting of organic acids + water are possible candidates to participate in the early growth of freshly nucleated particles. All the measured surface tensions and densities were fitted with equations, thermodynamically consistent if possible, to be easily applied to atmospheric model calculations of nucleation and subsequent evolution of particle size.

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List of publications

This thesis consists of an introductory review, followed by six research articles. The papers are reproduced with the kind permission of the journals concerned.

I A.-P. Hyvärinen, H. Lihavainen, Y. Viisanen, and M. Kulmala, Homogeneous nucleation rates of higher n -alcohols measured in a laminar flow diffusion chamber, *Journal of Chemical Physics* 120, 24, 11621, 2004.

II D. Brus, A.-P. Hyvärinen, V. Ždímal, and H. Lihavainen, Homogeneous nucleation rate measurements of 1-butanol in helium: A comparative study of a thermal diffusion cloud chamber and a laminar flow diffusion chamber, *Journal of Chemical Physics* 122, 214506, 2005.

III A.-P. Hyvärinen, D. Brus, V. Ždímal, J. Smolík, M. Kulmala, Y. Viisanen and H. Lihavainen, The carrier gas pressure effect in a laminar flow diffusion chamber, homogeneous nucleation of n -butanol in helium, *Journal of Chemical Physics*, 124, 224304, 2006.

IV A.-P. Hyvärinen, T. Raatikainen, A. Laaksonen, Y. Viisanen, and H. Lihavainen, Surface tensions and densities of $\text{H}_2\text{SO}_4 + \text{NH}_3 + \text{water}$ solutions, *Geophysical Research Letters* 32, 16, L16806, 2005.

V A.-P. Hyvärinen, H. Lihavainen, K. Hautio, T. Raatikainen, Y. Viisanen, and A. Laaksonen, Surface tensions and densities of sulphuric acid + dimethylamine + water solutions, *Journal of Chemical and Engineering Data* 49(4), 917, 2004.

VI A.-P. Hyvärinen, H. Lihavainen, A. Gaman, L. Vairila, H. Ojala, M. Kulmala, and Y. Viisanen, Surface tensions and densities of oxalic, malonic, succinic, maleic, malic, and *cis*-pinonic acids, *Journal of Chemical and Engineering Data* 51, 1, 255, 2006.

1 INTRODUCTION

Aerosol is a mixture of solid or liquid particles suspended in air. Originally, the term aerosol was used as an analogue to the term hydrosol, which means particles suspended in a liquid. Aerosols in the atmosphere are very diverse in size, concentration and chemistry. Their size varies from a few nanometres to hundreds of micrometers. Their total number concentrations have been reported to be as low as $< 10 \text{ cm}^{-3}$ over Antarctica (Shaw, 1988), and as high as about 10^6 cm^{-3} in heavy traffic conditions (Kittelson *et al.*, 2004; Pirjola *et al.*, 2004). They can contain a diverse composition of sulphates, nitrates, ammonium, sea salt, organic material, crustal species, hydrogen ions and water (Seinfeld and Pandis, 1998). The residence time of particles in the atmosphere ranges from a few days to a few weeks, therefore aerosols appear very different at different locations around the world.

Aerosols are important in the atmosphere for several reasons. First of all, they serve as a media for atmospheric heterogeneous chemistry. For example, global ozone loss can be attributed to heterogeneous chemistry in the midlatitude stratosphere (Seinfeld and Pandis, 1998). Aerosols also contribute to the radiative balance of the atmosphere, both directly and indirectly. The direct effect is via scattering and absorption of solar radiation (Seinfeld and Pandis, 1998; Twomey, 1991). The indirect effect is by aerosol particles acting as cloud condensation nuclei, thus influencing the albedo and life-time of clouds (Twomey, 1974; Albrecht, 1989; Lohmann and Feichter, 2005). In addition, aerosols affect human health; high levels of ambient particulate matter have been reported to be associated with public health effects in epidemiological literature (Dockery *et al.*, 1993; Katsoyanni *et al.*, 1997; Pope *et al.*, 2002; Davidson *et al.*, 2005). High particle concentrations can also lower the visibility considerably.

Particles are produced into the atmosphere either directly from natural or anthropogenic emissions (primary particles), or by gas-particle conversion (secondary particles). Secondary particle formation, or nucleation, events have been observed almost all around the world (Kulmala *et al.*, 2004a). In these events, particles with the size of a few nanometres appear and grow to larger sizes. Typical formation rates of 3 nm particles are in the range of $0.01\text{-}10 \text{ cm}^{-3} \text{ s}^{-1}$ and typical growth rates in the range of $1\text{-}20 \text{ nm h}^{-1}$. There is still no full understanding of all details of the nucleation events, although their appearance and development can be predicted to some extent with the knowledge of the prevailing circumstances (Anttila *et al.*, 2004; Korhonen *et al.*, 2004; Gaydos *et al.*, 2005; Jung *et al.*, 2006). New particle formation can lead to a significant increase in the number concentration of cloud condensation nuclei (e.g. Lihavainen *et al.*, 2003; Tunved *et al.*, 2006), therefore reliable theories and models for particle formation are required.

The term nucleation refers to the first step of a first order phase transition, e.g. transition between the solid, liquid and gas phase. This thesis concentrates solely on vapour to liquid nucleation. Conventionally, nucleation can be divided into homogeneous or heterogeneous processes. Homogeneous nucleation, or self-nucleation, happens without any pre-existing surfaces. In the case of heterogeneous nucleation, there is a surface, or a particle, on which the vapour molecules nucleate. Heterogeneous nucleation is usually

more favourable than homogeneous nucleation. For example pure water would not nucleate without pre-existing particles in atmospheric conditions.

The aim of this thesis is to gain insight to the formation of atmospheric particles from condensable gases from an experimental point of view. It will be shown in the following chapters that laboratory experiments on both nucleation and on physicochemical properties related to atmospheric particles are desired to do this. This study had the following individual goals:

- (1) To measure reliable nucleation rate data for verification of nucleation theories and parameterizations.
- (2) To consolidate the differences found in experimental nucleation rate measurements between different experimental devices.
- (3) To find out why nucleation rate measurements with diffusion based devices exhibit the so called carrier gas pressure effect.
- (4) To measure reliable surface tension and density data of compounds involved in the nucleation and growth of particles, or those involved in cloud droplet activation.
- (5) To parameterize the measured surface tension and density data in a form applicable to computational models of atmospheric processes.

2 THEORY OF VAPOUR TO LIQUID NUCLEATION

2.1 Thermodynamic aspects

The thermodynamics of vapour to liquid nucleation are based on the work by William Thompson (1870 and 1871). Later, J. W. Gibbs formulated the thermodynamic relations for systems in equilibrium with curved surfaces (Gibbs, 1961). These developments can be found in many basic text books (e.g. Seinfeld and Pandis 1998). Unless otherwise stated, the equations in this chapter follow the presentation of Seinfeld and Pandis (1998). Phase transition from pure vapour to liquid is accompanied with a change in the Gibbs free energy, ΔG :

$$\Delta G = G_{liquid} - G_{vapour} \quad (2.1)$$

This may be written with the help of thermodynamic potentials of the systems as:

$$\Delta G = (n_v g_v + n_l g_l + 4\pi r^2 \sigma) - (n_v + n_l) g_v = n_l (g_l - g_v) + 4\pi r^2 \sigma \quad (2.2)$$

where n is the number of molecules, g is the Gibbs free energy of a molecule, and subscripts l and v denote to liquid and vapour, respectively. Term $4\pi r^2 \sigma$ is the free energy associated with the surface of the droplet; r is the radius of the droplet and σ is the surface tension. To solve the term $(g_l - g_v)$, thermodynamic relation for the Gibbs free energy change is needed:

$$dG = -S_e dT + V dP + \sum_{i=1}^k \mu_i dn_i \quad (2.3)$$

where S_e is entropy, T is temperature, V is volume, P is pressure, and μ is chemical potential. At constant temperature and for one molecule this reduces to:

$$(g_l - g_v) = (V_l - V_v) dp = -V_v dp, \quad \text{since } V_v \gg V_l \quad (2.4)$$

Using the ideal gas law and integrating from equilibrium vapour pressure p_e to actual partial vapour pressure p_0 , we get

$$(g_l - g_v) = -kT \ln \frac{p_0}{p_e} \quad (2.5)$$

where $p_0/p_e =$ saturation ratio S (not to be mixed with entropy, S_e in eq. 2.3), and k is the Boltzmann constant. Substituting this into eq. (2.2) gives

$$\Delta G = 4\pi r^2 \sigma - n_l kT \ln S \quad (2.6)$$

It can be seen that the change in the Gibbs free energy is dependent on two terms. The first term arises from surface free energy and represents an increase in the chemical potential. The second term is the volume free energy of a cluster and represents a decrease in the chemical potential due to formation of a cluster. The change of the Gibbs free energy as a function of the radius of the droplet is presented in Figure 2.1. Three curves are presented in the figure; assuming $S < 1$, $S = 1$, and $S > 1$. It can be seen that minimum energy can be reached by increasing the cluster radius only when $S > 1$, i.e. when the vapour is supersaturated. If the supersaturation criterion is fulfilled, the growing cluster still needs to surmount an energy barrier. At the top of the energy barrier, the system is in a metastable state. The cluster in the metastable state is said to have a critical size. A smaller cluster would decay back to vapour phase, a larger cluster would grow spontaneously. The critical radius may be written as:

$$r^* = \frac{2\sigma v_l}{kT \ln S} \quad (2.7)$$

where v_l is the molecular volume of the liquid. This is the so called Kelvin -, or Gibbs-Thompson equation.

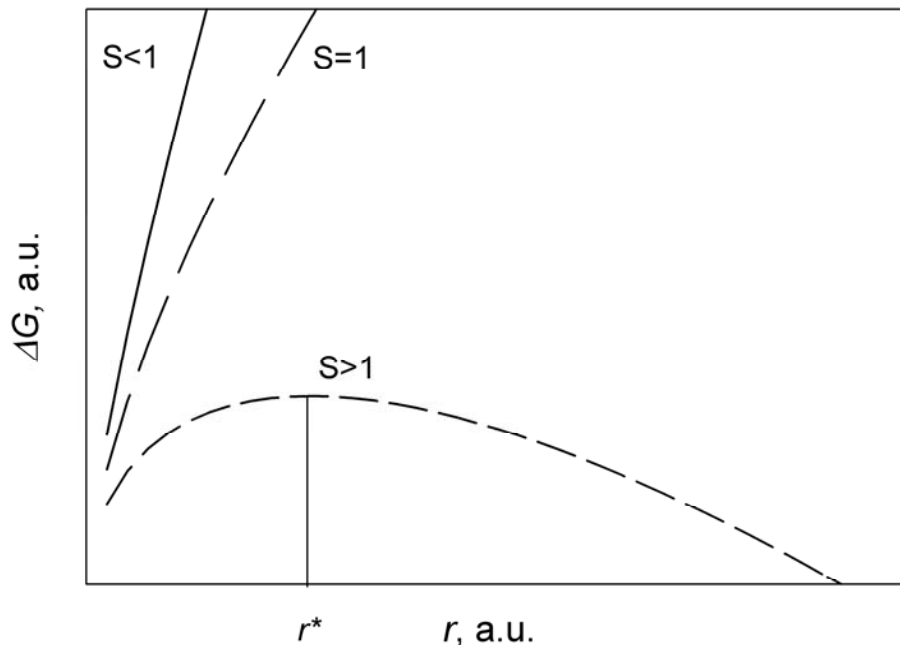


Figure 2.1 The change of the Gibbs free energy, ΔG as a function of the radius, r of the droplet. At the top of the energy barrier, r^* is the critical cluster size.

2.2 Kinetic treatment of nucleation rate: the classical nucleation theory (CNT)

While chapter 2.1 presented early thermodynamics by Thompson and Gibbs, the formulation of nucleation rate was later introduced by Becker and Döring (1935). Their

work is based on the kinetic treatment of growing clusters. A set of rate equations defines the concentration of different sized clusters as a result of the gain or loss of single cluster monomers. The number concentration of a cluster containing i monomers, N_i , changes with a rate of:

$$\frac{dN_i}{dt} = \beta_{i-1}N_{i-1}(t) - \gamma_i N_i(t) - \beta_i N_i(t) + \gamma_{i+1}N_{i+1}(t) \quad (2.8)$$

where β_i is the forward rate constant for the condensation of a monomer to a cluster with size i , and γ_i is the reverse rate constant for the evaporation of a monomer from a cluster with size i . A flux $J_{i+1/2}$ between cluster sizes i and $i+1$ can be written by:

$$J_{i+1/2} = \beta_i N_i - \gamma_{i+1} N_{i+1} \quad (2.9)$$

At steady state the flux is the nucleation rate and it is equal for all i 's. The nucleation rate is given by

$$J = N_1 \left(\sum_{i=1}^{\infty} \frac{1}{\beta_i f_i} \right)^{-1} \quad (2.10)$$

with the equilibrium constant

$$f_i = \prod_{j=1}^{i-1} \frac{\beta_j}{\gamma_{j+1}} \quad (2.11)$$

The equilibrium constant f_i is related to the formation of an i -sized cluster from isolated molecules. The nucleation rate J can therefore be expressed as a function of the equilibrium and forward rate constants. The forward rate constant β_i can be obtained from the kinetic theory of gases assuming that all the monomer-cluster collisions will lead to an enlargement of the cluster:

$$\beta_i = \frac{4\pi r^2 p}{\sqrt{2\pi m k T}} \quad (2.12)$$

where m is the mass of the vapour molecule and p is the total pressure. In the classical nucleation theory the equilibrium constant f_i takes a form of (Laaksonen *et al.*, 1995)

$$f_i = e^{(-\Delta G_i / kT)} \quad (2.13)$$

with the change in free energy (Oxtoby, 1992):

$$\Delta G_i / kT = \sigma A_i - i \ln S = \theta i^{2/3} - i \ln S \quad (2.14)$$

where A_i is the surface area of an i -sized cluster and θ is the dimensionless surface tension:

$$\theta = (36\pi)^{1/3} \sigma v_l^{2/3} / kT \quad (2.15)$$

Finally, after some mathematical manipulations, the nucleation rate formulated by Becker and Döring, J_{BD} , will have the following analytical expression:

$$J_{BD} = \left(\frac{2\sigma}{\pi m} \right)^{1/2} \left(\frac{p}{kT} \right)^2 v_l \exp \left(- \frac{16\pi v_l^2 \sigma^3}{3(kT)^3 (\ln S)^2} \right) \quad (2.16)$$

The nucleation rate equation proposed by Becker and Döring is not thermodynamically consistent as the cluster distribution does not follow the law of mass action. Nevertheless, the formulation leading to eq. (2.16) is typically known as the classical nucleation theory, and J_{BD} is widely used as the nucleation rate from classical theory. The inconsistency has been later corrected by Cortney (1961). The corrected nucleation rate, J_{Co} , is:

$$J_{Co} = \frac{1}{S} J_{BD} \quad (2.17)$$

Equation (2.17) is sometimes also called the classical nucleation theory or the revised CNT. Therefore, it should be warned that the term ‘‘CNT’’ might not be unambiguous in the literature. The term CNT used throughout this thesis refers to eq.(2.16), J_{BD} . In the framework of this thesis, it is worth pointing out that surface tension plays an integral role in equation (2.16). The nucleation rate increases with decreasing surface tension.

2.2.1 Assumptions of the CNT

It is important to point out that the formulation of the classical nucleation theory involves a numerous set of assumptions which may or may not be important at certain conditions (Vehkamäki, 2006). The main assumptions are presented in this chapter. First of all, the classical nucleation theory assumes 1) ideal gas and 2) incompressible liquid. In multicomponent cases, 3) an ideal mixture of gases is also assumed. It is also assumed that there is an abundant amount of the initial vapour, i.e. that 4) the pressure and composition of the vapour does not change during the nucleation process. More serious assumptions result from the capillarity approximation which assumes that the properties of a small cluster are the same as those of a bulk liquid. This means that 5) the surface tension is assumed to be that over a flat surface, and 6) the volume of a cluster is calculated from bulk liquid density. In the classical droplet model, 7) the surface dividing gas and liquid must fulfil the condition

$$\frac{d\sigma^*}{r^*} = 0 \quad (2.18)$$

This choice is called the surface of tension. Due to the independence of surface tension on curvature, 8) the surface of tension must also be located at the equimolar surface. In a multicomponent case this is a dubious choice, especially for surface active systems. The rest of the assumptions are a result of the derivation of the thermodynamic equations. It is assumed that 9) entropy does not change during the nucleation process. Also, in a multicomponent case, 10) the chemical potential of the surface is assumed to be the same as the chemical potential of the bulk liquid, and dependent on the liquid pressure and composition only.

2.3 Theory vs. experiment, nucleation rates of water

The classical nucleation theory is still the most widely used theory of nucleation, as it is easy to use and despite the numerous assumptions gives qualitatively correct nucleation rates as will be seen in this chapter. However, due to the several limitations, it is evident that the CNT should be tested in laboratory conditions against several compounds in different temperatures, saturation ratios and nucleation rate ranges. An example of the predictive power of the CNT can be given by comparing it to the measured nucleation rates of water. This is illustrated in Figure 2.2, where the nucleation rate J is presented as a function of saturation ratio S . It can be seen that that the CNT predicts the saturation ratio dependence of the experimental results (Wölk and Strey 2001) quite well, but it can not grasp the correct temperature dependence. At 220 K the CNT underestimates the nucleation rates by over one order of magnitude; at 260 K it overestimates them by about one order of magnitude. The temperature dependence has been observed to be wrong also with other nucleating systems, and often the deviation from experiment is more serious than in the case of water. However, the sign of the difference in temperature dependence is not necessarily the same.

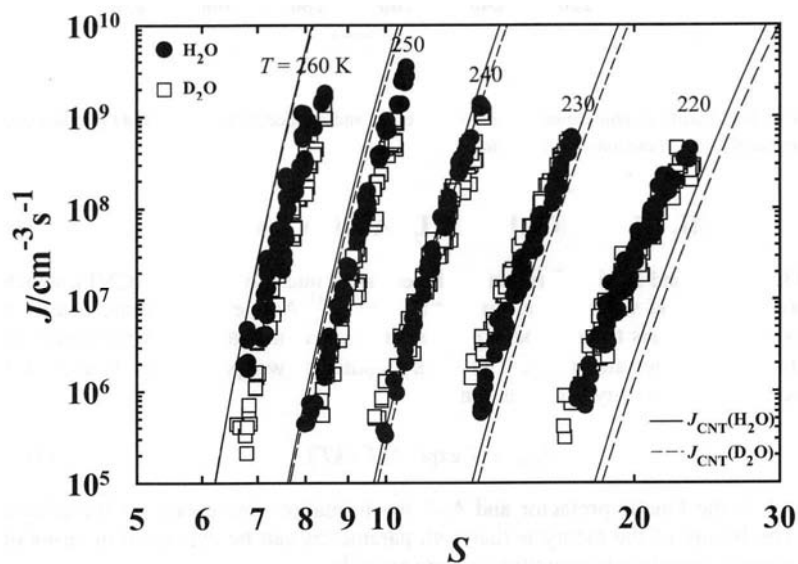


Figure 2.2 Nucleation rate J , as a function of saturation ratio, S , for water, H_2O and heavy water, D_2O . Figure from (Wölk and Strey, 2004).

3 ATMOSPHERIC NEW PARTICLE FORMATION

Vapour to liquid nucleation is the initiating step of atmospheric new particle formation which is observed frequently in several locations around the world (Kulmala *et al.*, 2004a). As the theory of nucleation is still not fully understood, accurate predictions of secondary particle formation in the atmosphere are hard to make. An example of a nucleation event is illustrated in Figure 3.1, where one day particle size distribution data measured with a differential mobility particle sizer-system at Pallas–Sodankylä Global Atmosphere Watch (GAW) station, Sammaltunturi site is shown.

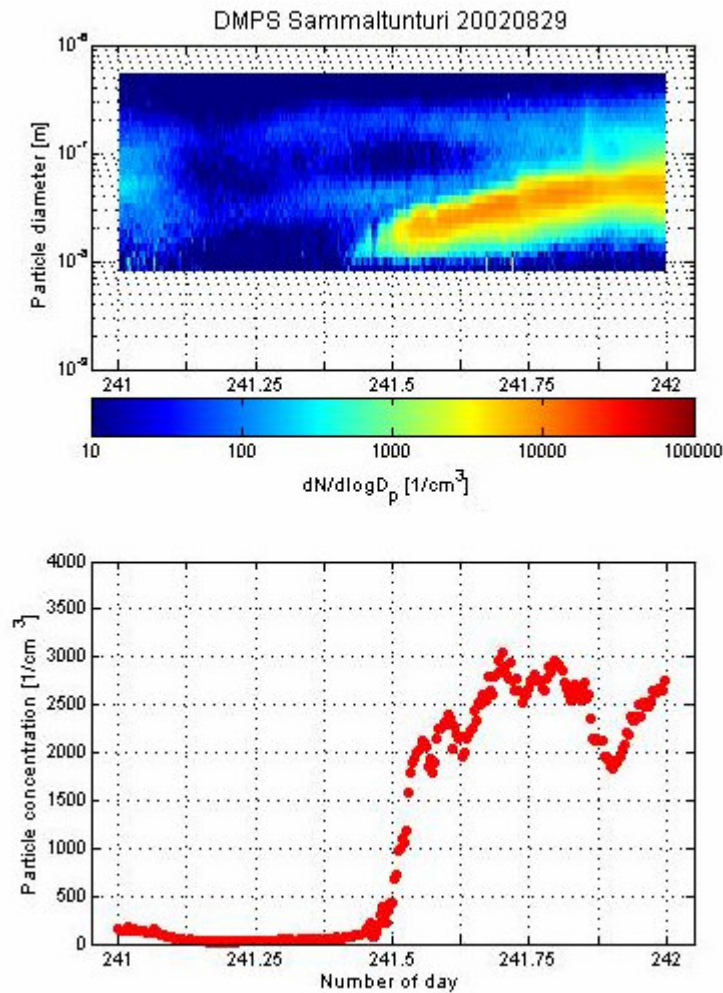


Figure 3.1 A new particle formation event observed at Sammaltunturi, Pallas, on 29.8.2002. Upper figure: particle size distribution as a function of time. Lower figure: total particle concentration as a function of time.

According to the current understanding, new particle formation is likely to involve two stages. The first stage produces thermodynamically stable clusters around 1 nm via nucleation (Kulmala *et al.*, 2000), and in the second stage the stable clusters grow by

condensation and coagulation (Kulmala, 2003; Kulmala *et al.*, 2006). The present instrumentation allows detection of neutral particles larger than 3 nm, and thereby nucleation mechanisms can not be probed directly. Only such formation events are observed when the clusters grow to sizes larger than 3 nm. Thus, to understand new particle formation mechanisms, it is also important to understand the initial growth of atmospheric particles from 1 nm to 3 nm.

3.1 Nucleation in the atmosphere

While one component homogeneous nucleation is unlikely to happen in the atmosphere, two –or three component nucleation is much more probable. The most studied example is the binary nucleation of sulphuric acid and water (Nilsson and Kulmala, 1998; Vehkamäki *et al.*, 2002), as sulphuric acid has a very low equilibrium vapour pressure above water solution. Typical atmospheric concentrations of gaseous sulphuric acid exceed its saturation vapour pressure. Sulphate aerosols are also found in large quantities in both stratosphere and the troposphere. In some extreme conditions the observations are consistent with the binary sulphuric acid + water nucleation (Clarke *et al.*, 1998; Weber *et al.*, 1999). However in the boundary layer, the observed particle formation rate often exceeds that predicted from the atmospheric concentrations by binary $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$ nucleation alone (Weber *et al.*, 1998; Kulmala *et al.*, 2001; O’Dowd *et al.*, 2002). This has led to a conclusion that there may be other species involved in the nucleation scheme, such as ammonia which is abundant in the atmosphere and can lower the vapour pressure of H_2SO_4 above a water solution. Ternary nucleation of sulphuric acid + ammonia + water is nowadays widely accepted as one of the main possible pathways of producing thermodynamically stable clusters. Other suggested mechanisms to explain observed atmospheric nucleation are nucleation of organic vapours (Marti *et al.*, 1997; Zhang *et al.*, 2004), ion-induced nucleation (Yu and Turco, 2001; Laakso *et al.* 2002), and halogen-oxide nucleation (Hoffmann *et al.*, 2001).

Atmospheric nucleation is still predicted mostly with classical thermodynamics and the classical nucleation theory. Knowing the limitations of the CNT, it seems evident that the calculated atmospheric nucleation rates will contain some uncertainty. However, the CNT is used due to the rather simple input parameters needed in the theory. As seen in the previous chapter, only macroscopic values of the liquid density, surface tension and saturation vapour pressure are needed. If these are known for all chemical compositions of the bulk liquid at wanted temperatures, sizes of the critical clusters and nucleation rates can be predicted. Model calculations predict that ternary nucleation of sulphuric acid + ammonia + water happens at most conditions occurring in the boundary layer during daytime (Kulmala *et al.* 2000). This finding illustrates that nucleation is probably not the limiting step in atmospheric new particle formation.

Sometimes the sulphuric acid + ammonia + water nucleation rates predicted with the measured atmospheric vapour concentrations exceed the kinetic limit of nucleation, which is an unphysical prediction (Boy *et al.* 2005). It has been suggested that the too high nucleation rates are predicted because ammonium bisulphate formation during nucleation process is not taken into account in the calculations (Anttila *et al.* 2005). If

this formation is taken into account however, the observed nucleation rates are underestimated. This finding suggests that there may also be other nucleation pathways in the atmosphere.

3.2 Initial growth of nucleated particles

Ternary nucleation of sulphuric acid + ammonia + water may be sufficient to explain the rates of atmospheric nucleation, and in some cases, the concentrations of these vapours are enough to account for the growth of particles to three nanometre and larger sizes (Jung *et al.*, 2006). However, in many circumstances, other vapours like organic ones are needed to explain the initial growth of the nucleated particles, suggesting that nucleation and growth may be decoupled (Kulmala *et al.*, 2000). According to very recent studies, cluster activation is a strong candidate to explain the growth, as it reproduces the linear dependence observed between formation rate of 3 nm particles and sulphuric acid concentration (Kulmala *et al.*, 2006). There are several ways for activation processes to take place (Kulmala 2004b), e.g. heterogeneous reactions, polymerization, heterogeneous nucleation, multicomponent nano-Köhler theory (Kulmala *et al.*, 2004c), and charge enhanced nucleation.

The growth rates observed during atmospheric nucleation events have been found consistent with the proposed nano-Köhler growth mechanism, in which multicomponent water soluble organic vapours condense on a thermodynamically stable cluster as it grows past an activation diameter (Kulmala *et al.*, 2004c). The nano-Köhler theory is analogous to the traditional Köhler theory which describes the activation of water soluble aerosols into cloud droplets (Köhler, 1936). The models utilizing the nano-Köhler theory capture the qualitative features of the particle size distribution dynamics well (Korhonen *et al.* 2004) and are able to explain the observed seasonal cycle in the number of new particle formation events in a boreal forest site (Anttila *et al.* 2004).

Surface tension of organic compounds is an integral input parameter in the Kelvin-term of the nano-Köhler theory, and this also contains an uncertainty in the nano-Köhler theory. Actual organic compounds involved in the growth of the freshly-nucleated particles have not been identified, and the knowledge of their physicochemical properties is sparse. Measuring physicochemical properties such as surface tension and density for a wide variety of organic species is therefore desired.

4 EXPERIMENTAL NUCLEATION RATE MEASUREMENTS

Experimental nucleation measurements date back to Wilson (1897, 1900), who observed the heterogeneous nucleation of water in an expansion cloud chamber. Early nucleation studies were concentrated only in determining the saturation ratio at which nucleation was observed (the critical saturation ratio). Nowadays the demands for quantitative nucleation measurements have increased. According to Kashchiev (1982) and Anisimov and Cherevko (1985), isothermal nucleation rates measured as a function of saturation ratio yield the molecular content of critical clusters. Measuring isothermal nucleation rates has thus set a standard for nucleation measurements. For atmospheric purposes, nucleation rate measurements are desired in order to improve and validate nucleation theories used in predicting secondary particle formation.

4.1 Methods

Whatever the method for nucleation rate measurements is, the first pre-requisite is to produce a supersaturation of the nucleating vapour. In principle, there are three ways of doing this: non-isothermal diffusion, adiabatic expansion and turbulent mixing. There are over twenty different devices utilized by nucleation investigators (Heist and He, 1994). In the following sub-chapters the most commonly used devices are introduced.

4.1.1 The laminar flow diffusion chamber (LFDC)

The nucleation rate measurements in this thesis (**Papers I-III**) were mostly conducted with a laminar flow diffusion chamber originally built by Lihavainen and Viisanen (2001). The operation principle of the laminar flow diffusion chamber is based on non-isothermal diffusion. The method was first utilized by Anisimov *et al.* (1978), and has later been adopted by several researchers (e.g. Hämeri *et al.*, 1996; Vohra and Heist 1996; Lihavainen and Viisanen, 2001, Mikheev *et al.*, 2002).

The LFDC is presented in Figure 4.1 in the form it was used for pressure dependent measurements in **Paper III**. The LFDC consists of three main parts, all of which are separately temperature-controlled. A flow of a carrier gas is first brought into a saturator, a horizontal tube half-filled with the nucleating substance. The carrier gas gets fully saturated with the vapour of the substance in the saturator. The vapour-gas mixture then continues to flow through the preheater and the condenser, two co-axial vertical tubes with the same inner diameter. The preheater is kept at a higher temperature than the saturator. It assures that the flow becomes laminar with a known velocity profile. It also defines the boundary and initial temperature for the mixture before it enters the condenser. The condenser is at a much lower temperature than the saturator. The nearly step-wise temperature drop leads to an increase in the saturation ratio of the vapour, and nucleation is observed if critical saturation ratio is exceeded. The mixture remains supersaturated long enough to allow nucleated particles to grow to an optically detectable size. Different versions of the LFDC are able to produce nucleation rates ranging from 10^3 to 10^8 $\text{cm}^{-3}\text{s}^{-1}$. With a few exceptions (Anisimov *et al.*, 1998; Anisimov *et al.*, 2000; **Paper III**), all the measurements have been made near atmospheric pressure.

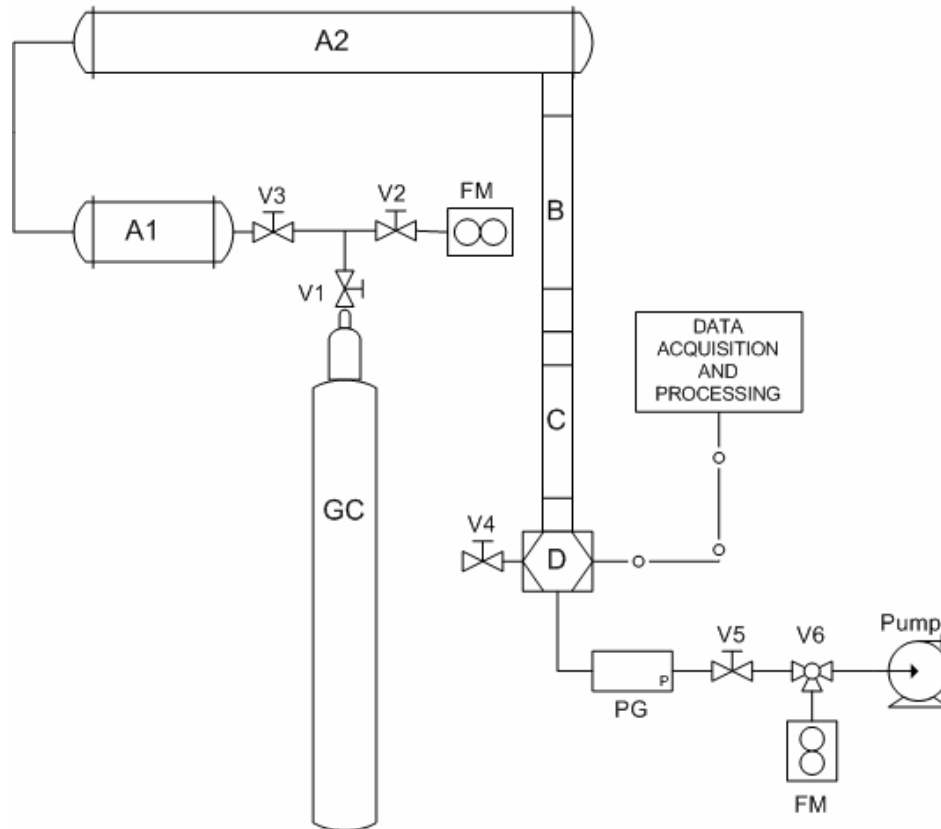


Figure 4.1 A schematic figure of the LFDC for nucleation rate studies: A1 – presaturator, A2 – saturator, B – preheater, C – condenser, D – optical cell, FM – flow meter, GC – gas container, PG – pressure gauge, V1-V6 – valves.

4.1.2 Other experimental devices

The variety of different experimental devices creates a wide scale of nucleation rates that can be measured. This is seen in Figure 4.2, where the different methods and their measurable nucleation rates are presented. Devices measuring the lower end of the nucleation rate window are thermal diffusion cloud chambers (TDCC). With TDCC's, nucleation rates ranging from 10^{-3} to $10^2 \text{ cm}^{-3}\text{s}^{-1}$ can be measured (e.g. Katz, 1970, Ferguson *et al.*, 2001; Brus *et al.*, 2006). Quite similar in principle to the LFDC, thermal diffusion cloud chambers also rely on non-isothermal diffusion of vapour. However, nucleation inside a TDCC happens in a static carrier gas–vapour mixture instead of a flowing system.

The other commonly used nucleation devices generally utilize the adiabatic expansion method. Nucleation rates ranging from 10^2 to $10^5 \text{ cm}^{-3}\text{s}^{-1}$ can be measured with single piston expansion chambers (e.g. Schmitt *et al.*, 1982; Schmitt and Doster, 2002). Piston expansion wave tubes are used to measure nucleation rates between 10^4 and $10^9 \text{ cm}^{-3}\text{s}^{-1}$ (Graßmann and Peters, 2000 and 2002). The same nucleation rate range can be achieved with nucleation pulse chambers (Wagner and Strey, 1984; Viisanen *et al.*, 1994; Iland *et al.*, 2004). Slightly higher nucleation rates, ranging from 10^8 to $10^{11} \text{ cm}^{-3}\text{s}^{-1}$ are measured

with shock tubes (Luijten *et al.*, 1997; Holten *et al.*, 2005). The highest achievable nucleation rates, $10^{15} - 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$, are measured with supersonic nozzles (Kim *et al.* 2004; Gharibeh *et al.*, 2005).

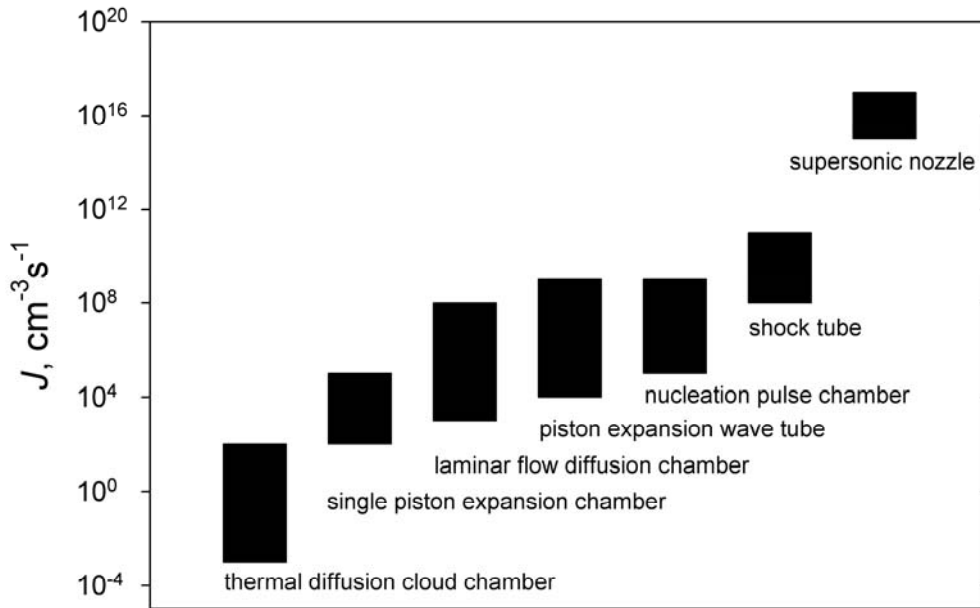


Figure 4.2 Experimental devices for nucleation rate measurements and their nucleation rate ranges.

4.2 Nucleation rates measured in different devices

The nucleation rates measured in different experimental devices have always been difficult to compare. This is because the conditions of the measurements are highly dependent on the nature of the particular device. As seen in Figure 4.2, already the measurable nucleation rates do not always overlap. Also the substances which can be measured depend on the nature of the device. Other variables that depend on the measuring device are temperature, total pressure and carrier gas type. Another source of uncertainty in the chamber-devices relying on the non-isothermal diffusion principle are the transport properties used to model the temperature and partial vapour pressure in the chamber. Unless the same definitions of the transport properties are used, the measured results may differ considerably.

4.2.1 The Joint Experiment on Homogeneous Nucleation

Given the complicatedness of comparing nucleation rate results, it was decided during *Workshop on Nucleation Experiments –State of the Art and Future Developments 1995* in Prague that there should be a joint experiment on homogeneous nucleation. The following details were chosen for the experiment (Smolík and Wagner, 1996): The nucleating substance was agreed to be *n*-pentanol which was provided from one lot. Nucleation temperatures were chosen as 240 K – 260 K. Helium was chosen as a carrier

gas with a total pressure of about 100 kPa. Also, a common set of transport properties were provided by Ždímal and Smolík (1996). During recent years, these measurements have been performed by several research groups and a considerable set of data is available. The results obtained for the joint experiment are presented in Figure 4.3. The results have been scaled using the classical nucleation theory. This way, results measured at the different nucleation rate ranges can be normalized.

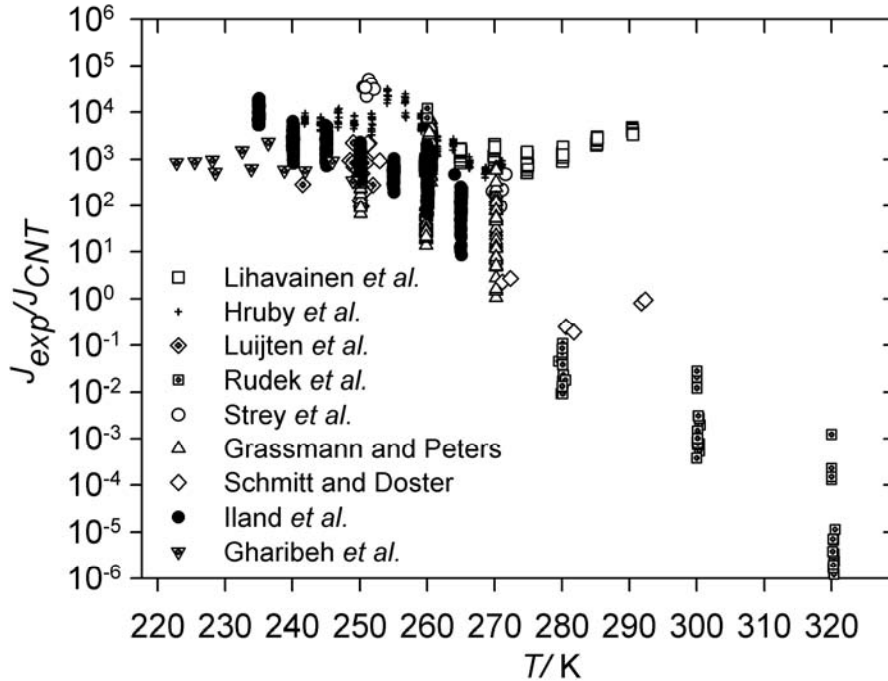


Figure 4.3 Ratio of *n*-pentanol experimental nucleation rates, J_{exp} and nucleation rates predicted by the classical nucleation theory, J_{CNT} as a function of temperature T .

The results between different devices agree with each other reasonably well at the original temperature range of 240–260 K chosen for the joint experiment. However, the temperature dependence of the nucleation rates can be very different in different devices, resulting in more than four orders of magnitude difference in nucleation rate at the same nucleation temperature outside this temperature range. It is evident that the operation characteristics and data evaluation in different devices have to be considered more carefully in order to explain such differences in data.

4.2.2 Comparison of diffusion based devices

While comparable data of different devices is increasing thanks to the joint experiment, there are very few studies directly comparing different experimental devices. In this thesis, work was done to understand the behaviour of the two diffusion based devices, the laminar flow diffusion chamber and the thermal diffusion cloud chamber, yielding considerably different nucleation rates despite having a similar basic principle (**Paper II**). It is thought that accurate temperature measurements are the most delicate point of operation in these devices, together with accurate transport parameters during data

evaluation. It was shown that implementing unlikely large uncertainties in these temperature measurements was not enough to explain the different results. It should be noted that using the Hale's scaling formalism (Hale, 1986 and 1992), the *n*-pentanol nucleation rates measured in the LFDC (Lihavainen *et al.*, 2001) are in good agreement with results from other devices, whereas nucleation rates measured in the TDCC (Rudek *et al.*, 1999) deviate from the scaling law (Gharibeh *et al.*, 2005).

4.2.3 Pressure effect in nucleation measurements

One of the discrepancies between different experimental techniques concerns the carrier gas effect. Inert carrier gas has been used in experimental nucleation studies mainly as a latent heat reservoir, i.e. to maintain the nucleating clusters in isothermal conditions (e.g. Wyslouzil and Seinfeld, 1992). Typically the existence of the carrier gas is neglected. However, several experimental and theoretical studies implicate that both the type and pressure of the carrier gas can affect the measured nucleation kinetics in a multitude of ways (Brus *et al.* 2006). The effect of carrier gas pressure on nucleation rates has been mostly observed in diffusion based measurements. The negative pressure effect in TDCC's has been observed in nucleation conditions near atmospheric pressures and at high pressures. (Brus *et al.*, 2006; Heist *et al.*, 1994 and 1995) A similar effect was also observed in **Paper III**. A positive pressure effect was found for the nucleation of *n*-pentanol + helium with total pressures ranging from 100 to 300 kPa in a LFDC (Anisimov *et al.*, 2000). In devices applying adiabatic expansion, no pressure effect has been observed (Viisanen *et al.*, 1993; Viisanen and Strey, 1994), or it has been identified as something else than related to nucleation itself (e.g. Graßmann and Peters, 2000).

From an experimental point of view it is important to first rule out any measurement related inaccuracies and artefacts to explain for the pressure effect. Several such reasons have been taken into account when analyzing results obtained with the TDCC and the LFDC (Brus *et al.*, 2006; **Paper III**), but no conclusive evidence have been found to explain for the appearance of the pressure effect. It is therefore necessary that more systematic studies of the carrier gas pressure effect will be made to understand whether the effect is real or an artefact of these particular devices.

4.3 Systematic nucleation rate studies

A powerful way of identifying experimental inaccuracies is to measure extensive sets of nucleation rates of substances with similar properties (Strey *et al.*, 1986; Rudek *et al.*, 1996; Rusyniak *et al.* 2001; Rusyniak and El-Shall, 2001; **Paper I**). Quite often they exhibit the same temperature dependence, and their deviations from theoretical predictions are systematic or close to each other. In the case of LFDC's it was shown (**Paper I**) that systematic nucleation behaviour of an alcohol series is highly dependent on the definitions of the equilibrium vapour pressure used during data analysis. The equilibrium vapour pressures which have not been measured with an adequate accuracy, or have to be extrapolated to correct temperatures, will yield a serious inaccuracy to nucleation rates measured in a LFDC.

When experimental inaccuracies have been eliminated, the measurements of substances with similar properties are desirable in testing different nucleation theories. Patterns in nucleation behaviour can also be shown, and theory independent scaling laws can be developed. For example, Nadykto and Yu (2005) were able to predict the nucleation rates of a wide variety of species with a surprising accuracy by applying a rather simple empirical correction factor to the classical nucleation theory. A systematic study with similar nucleating substances could also bring light to the carrier gas pressure effect.

5 SURFACE TENSION AND DENSITY MEASUREMENTS

Measurements of both surface tension and density were conducted in the work for this thesis. The knowledge of these physicochemical properties is essential when modelling the nucleation and growth of atmospheric particles. Moreover, this kind of data is scarce for atmospherically important substances. The main focus was in the measurements of surface tension. The work needed to change the surface area of a liquid (or a solid) is defined by

$$dW = \sigma dA \quad (5.1)$$

where dW is the work done, σ is the surface tension and dA is the change of the surface area. At constant volume and temperature this is the same as the change of Helmholtz free energy. Because the Helmholtz energy decreases as the surface area decreases, it is energetically profitable to minimize surface area. This is why droplets tend to be spherical: sphere is a form with the smallest surface to volume ratio.

Surface tension is a key parameter whenever a new surface is formed, for example during vapour to liquid nucleation. In the previous chapters it has also been shown that surface tension plays a role in the growth of freshly nucleated particles. In fact, surface tension is an important parameter in several processes involving atmospheric aerosols. Such processes include the formation of cloud condensation nuclei and activation of particles into cloud droplets. The surface tension measurements conducted for this thesis are focused on substances which may be responsible for nucleation and early growth of particles, but the same compounds may be important in the other atmospheric processes as well, making the measurements useful from many points of view.

While density is easily deemed as a less interesting parameter than surface tension, it is also an important property needed in atmospheric model calculations. The density can be used in deriving the partial molecular volumes of different components in solutions, which are needed in the Kelvin equation.

5.1 Methods

Surface tensions of small aerosol particles may be very different from those of the corresponding bulk liquid due to the curvature effect on surface tension. However, measuring the surface tensions of such small particles is practically impossible with current technology, and it is common to measure the surface tensions as a macroscopic quantity. Densities, on the other hand, are typically needed as macroscopic quantities. There are several methods available for measuring surface tensions and densities of bulk liquids.

5.1.1 Surface tension measurements: The Wilhelmy plate method

In the work for this thesis, the surface tensions were measured with the Wilhelmy plate method (Wilhelmy, 1863). The method is based on a force measurement of the surface. A

vertically suspended platinum plate with known geometry is lowered to a bulk sample liquid, causing the surface tension to pull the plate into the sample. The plate is lifted back to zero position, and the force (weight of the surface) is measured. The surface tension can then be obtained from:

$$\sigma = \frac{F_w}{l_b \cos \theta} \quad (5.2)$$

where F_w is the measured force, l_b is the wetting length of the plate, and θ is the contact angle between the tangent of the wetting line and the plate surface. It is assumed that the plate is totally wetted, making the contact angle zero. The Wilhelmy plate method was chosen for the measurements, because it is easy to use and gives reproducible results for most compounds. The commercial tensiometer applied in the work for this thesis is presented in Figure 5.1. Another reason for choosing the Wilhelmy plate method is that the same, relative small volume sample can be reused for density measurements.



Figure 5.1. Digital Tensiometer K 10ST, Krüss GmbH, using the Wilhelmy plate method.

5.1.2 Surface tension measurements: Other methods

There are several different methods for measuring surface tensions. One of the oldest is the Du Noüy ring method (du Noüy, 1919), and similar to the Wilhelmy plate method it also utilizes a force measurement of the surface. Commercial devices quite often have the option of measuring either with the Wilhelmy plate- or the Du Noüy ring- method.

The capillary rise method is one of the simplest to measure surface tensions. In this method, a capillary tube is inserted into bulk liquid, and surface tension causes the liquid to rise in the capillary tube (Strey and Schmelting, 1982). The surface tension can be determined from the height of the liquid column formed in the capillary tube. Other methods include the spinning drop- and the pendant drop methods. They are based on the measurement of the drop diameter. The oscillating drop method coupled with a drop levitation system can be perceived as closest to measuring the surface tensions of tiny

droplets (Matsumoto *et al.*, 2001). Measuring surface tension this way also removes any external forces and contaminants affecting the measurement. However, the drop diameters measurable with such methods are still in the millimetre size and can be regarded as bulk measurements.

5.1.3 Density measurements

In principle, the density of a substance is easy to measure. There are several commercial applications available and nowadays these are commonly combined with surface tension devices. In the work for this thesis, density was determined as a weight/volume measurement of the bulk liquid directly after measuring the surface tension of the same sample. As the main focus of this work was in the measurements of surface tension, it is outside the scope of this thesis to review the methods of density measurements.

5.2 Physicochemical properties of nucleating species

The physicochemical data of compounds related to nucleation is scarce, especially concerning multi-component substances. The surface tensions and densities of some compounds relevant to nucleation which have been measured, are sulphuric acid + water (e.g. Myhre *et al.*, 1998) and sulphuric acid + ammonia + water (**Paper IV**). However, in order to explore alternative pathways of nucleation, physicochemical data of other potential candidate substances are needed. One of such is sulphuric acid + dimethylamine + water (**Paper V**). Dimethylamine has been found in a particulate phase in a boreal forest area during nucleation events and in the gas phase during other times (Kulmala *et al.*, 2001). The molecular structure and properties of dimethylamine are very close to those of ammonia, and may replace it in the ternary nucleation scheme. The surface tensions of some other ternary compounds containing sulphuric acid have been measured earlier, for example sulphuric acid + nitric acid + water (Martin *et al.* 2000).

5.3 Physicochemical properties of species involved in early growth

Physicochemical properties are also needed in estimating the initial growth of freshly nucleated particles. In this case, important substances are organic ones, and mixed organic + inorganic compounds. These may be the same compounds as measured for predicting activation of particles to cloud droplets. Unfortunately, the substances are present in totally different concentrations in these two processes. For cloud droplet activation, the concentrations of the substances are dilute, as most of the particles will contain a notable amount of water. Several surface tension measurements of such aqueous solutions of organics and organics + inorganics can be found in the literature (Shulman *et al.*, 1996; Tuckermann and Cammenga, 2004; Henning *et al.*, 2005; **Paper VI**). When it comes to nucleation and early growth of freshly nucleated particles, the picture is quite different: a newly formed particle may contain only tens of molecules meaning that the corresponding bulk concentrations should be very high. This is a problem from an experimental point of view, as the concentrations of several binary and ternary substances depend on their solubility and the maximum concentrations of their

individual constituents. For example, several organic acids found in the particulate phase in the atmosphere have a limited solubility in water at ambient conditions (**Paper VI**).

5.4 Properties at concentrations relevant to nucleation / early growth

Only a few studies have reported surface tensions of organic compounds at highly concentrated solutions (Álvarez *et al.*, 1997; Gaman *et al.* 2004; **Paper VI**). In the paper by Gaman *et al.* and in **Paper VI** also the densities are reported. Properties at high concentrations can be obtained by measuring substances which are present in pure liquid form in ambient conditions (Álvarez *et al.*, 1997), or theoretically by estimating the surface tension for the higher concentrations. The surface tensions of pure liquid compounds may be estimated for example by the Macleod-Sugden method (Gaman *et al.*, 2004; **Paper VI**), and the gap between the experiments and the pure compound surface tension may be interpolated using thermodynamically consistent functions of surface tension. A similar principle can be used in the case of density.

There are several methods available for modelling the surface tension. One of such is a thermodynamically consistent function proposed by Chunxi (2000), which is based on thermodynamic definition of surface tension and the expression of the Gibbs free energy:

$$\sigma = \sum_i x_i \sigma_i - RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \quad (5.3)$$

where x is the mole fraction, R is the Rydberg constant, A is surface area, and Λ is a dimensionless parameter related to the molar volumes of the components and to the difference in interaction energy between molecule pairs ij and ii . This may be fitted to measured data by using Λ and A as fitting parameters (**Papers IV and VI**). The fitted version of the Chunxi equation is able to reproduce the measured values accurately, as well as predict the gap between the measured values and the pure component value in a sensible way (**Paper VI**).

6 REVIEW OF THE PAPERS

The papers in this thesis can be divided in two categories: the ones concerning measurements of homogenous nucleation rates and the ones concerning measurements of surface tension and density. **Paper I** presents measurements of homogeneous nucleation rates for higher n -alcohols in a laminar flow diffusion chamber. **Paper II** compares two different measurement devices to measure homogeneous nucleation rates. **Paper III** investigates the carrier gas pressure effect in homogeneous nucleation studies, bringing the understanding of the effect in a laminar flow diffusion chamber to the same level as in the thermal diffusion cloud chamber. **Papers IV** and **V** present the surface tensions and densities of two ternary compounds which may participate in atmospheric nucleation events. **Paper VI** extends the same to aqueous organic substances found in atmospheric particulate matter.

Paper I presents nucleation rate measurements performed with a laminar flow diffusion chamber. Nucleation rate isotherms of n -butanol, n -pentanol, n -hexanol, n -heptanol, and n -octanol were measured using helium as a carrier gas. The measurements were made at temperatures of 250-310 K and at atmospheric pressure. Measurements of substances with similar molecular properties can be used to identify reasons for inaccuracies. The expression and accuracy of thermodynamic parameters, in particular equilibrium vapour pressure, were found to have a significant effect on calculated nucleation rates. The results were compared to the classical nucleation theory (CNT), the self-consistency corrected classical theory (SCC) and Hale's scaled model of the CNT. Best general agreement was found when Hale's scaled model was used. The saturation ratio dependence was predicted closest to experiment with the CNT. The nucleation rates were in reasonable agreement compared to those found in the literature. The molecular content of the critical clusters was calculated using the nucleation theorem resulting in a close agreement with the Kelvin equation.

Paper II is a comparative study of two diffusion based devices used to measure isothermal nucleation rates. The isothermal homogeneous nucleation rates of n -butanol + helium were measured simultaneously in a thermal diffusion cloud chamber and in a recently built laminar flow diffusion chamber. The chosen system n -butanol + helium could be studied reasonably well in both devices, in the overlapping range of temperatures. The aim of the study was to understand the experimental factors contributing to different results of the measuring devices. The same isotherms measured with the thermal diffusion cloud chamber occurred at higher saturation ratios of the devices. The temperature dependence was observed to be similar in both devices. The laminar flow diffusion chamber provided critical cluster sizes slightly above those estimated by the Kelvin equation; the thermal diffusion cloud chamber suggested critical cluster sizes significantly smaller. It was shown that even implementing an unrealistically large temperature uncertainty into the nucleation calculations could not explain the different results of the two devices.

Paper III introduces nucleation rate measurements in a laminar flow diffusion chamber at total pressures ranging from 50 kPa to 210 kPa to investigate the effect of carrier gas

pressure on nucleation. The measured nucleation rates of *n*-butanol + helium decreased as a function of increasing pressure. This negative carrier gas pressure effect is similar which has been found in thermal diffusion cloud chambers. The observed pressure effect was found to be temperature dependent. At nucleation temperature of 280 K and at the same saturation ratio, the maximum deviation between nucleation rates measured at 50 kPa and 210 kPa was about three orders of magnitude. At nucleation temperature of 265 K, the effect was negligible. Also the critical cluster sizes seemed to be dependent on the temperature. At 50 kPa, the critical cluster sizes were highest, and at 210 kPa the sizes were lowest. Operation characteristics of the laminar flow diffusion chamber at both under- and overpressure were determined to verify a correct and stable operation of the device. Several sources of inaccuracies were considered in the interpretation of the results: uncertainties in the transport properties, non-ideal behaviour of the vapour-carrier gas mixture and shortcomings of the mathematical model; none of which were found to be responsible for the observed pressure effect.

Paper IV presents the surface tensions and densities of inorganic sulphuric acid + ammonia + water solutions. This ternary compound is a popular candidate to participate in atmospheric nucleation events. The measurements were made at 25 °C. The ratios of the compounds in the mixture were limited by the concentrations of the original aqueous ammonia solution and salt formation during mixing of sulphuric acid and ammonia. The surface tension reached its highest value when the mole fraction ratio between ammonia and sulphuric acid was two, corresponding to the binary solution of ammonium sulphate + water. The results were presented in a form of polynomial functions which can be applied to atmospheric model calculations of nucleation and particle growth.

Paper V investigates the surface tensions and densities of aqueous solutions of dimethylamine and sulphuric acid at 25 °C. Dimethylamine is an organic compound which has been found in atmospheric particulate matter in boreal forests. It can replace ammonia in the ternary nucleation scheme mentioned in **Paper IV**. Surface tension of sulphuric acid + dimethylamine + water started to decrease when dimethylamine was added a sufficient amount to turn the solution alkaline. Dimethylamine was found to decrease the surface tension much more effectively than ammonia. This suggests that dimethylamine is a more powerful nucleating agent than ammonia. Polynomial fits were applied to measured data sets of both surface tension and density.

Paper VI turns the focus of the surface tension measurements to aqueous organic compounds. The surface tensions and densities of aqueous solutions of oxalic-, malonic-, succinic-, maleic-, malic-, and *cis*-pinonic acid were measured as a function of the acid mole fraction at 25 °C, and at a constant mole fraction of acids also as a function of temperature. These organic acids are typically found in atmospheric aerosols. The measurable mole fractions were limited by the solubilities of the acids. All the acids lowered the surface tension of pure water. *Cis*-pinonic acid lowered the surface tension most effectively. The measured surface tensions were fitted with equations covering the acid mole fraction range from zero to one, and assuming a theoretical surface tension of pure, supercooled acids at room temperature. The measured densities were also fitted in a

similar way. These equations can be used in model calculations of formation and growth of atmospheric particles.

7 CONCLUSIONS

Experimental nucleation rate data and physicochemical properties of nucleating compounds were measured in laboratory conditions to gain insight on new particle formation in the atmosphere. Homogeneous nucleation rate measurements of simple compounds are needed to understand the operational characteristics of nucleation devices, and to understand why measurements with different devices can give nucleation rates different by orders of magnitude. Results from the experiments can be used to evaluate nucleation theories which are used to predict nucleation in atmospheric conditions. Physicochemical properties of compounds related to new particle formation are needed in model calculations of nucleation and early growth of particles. An incomplete knowledge of such properties is often the major uncertainty which inhibits the accurate predictions of the roles of different compounds in atmospheric new particle formation.

This thesis has contributed to the understanding of nucleation and new particle formation in the atmosphere in the following way, answering the objectives given in the introduction:

(1) A laminar flow diffusion chamber (LFDC) was used to measure the nucleation rates of higher *n*-alcohols, producing a systematic nucleation rate study. It was pinpointed that the analysis of data given by the LFDC requires accurate thermodynamic data in order to produce reliable nucleation rates. If proper expressions of equilibrium vapour pressures are used, the LFDC yields reliable nucleation rates which can be used to evaluate nucleation theories.

(2) A comparative study of two diffusion based nucleation devices was made to investigate the reasons for different results generally given by the devices. The nucleation of *n*-butanol in helium was studied. Despite conducting the experiments in conditions as similar as possible, and attempting to consolidate the data with a considerable error analysis, the results still exhibited a notable difference in both position and slope of isothermal nucleation rates. This finding illustrates that more work has to be done to understand the operational characteristics of both of the devices.

(3) One of the most irritating phenomena in nucleation rate measurements has been the effect of total pressure on nucleation rates. This effect has only been seen in diffusion based devices. The LFDC was modified for measurements at different pressures and a pressure effect similar in thermal diffusion cloud chambers was revealed. For the first time, measurements were conducted below atmospheric pressure in a LFDC. Extensive error analysis did not explain the occurrence of the pressure effect. This conclusion has also been drawn in TDCC-studies. Unless the effect is real, this verifies that the operational characteristics of diffusion based nucleation devices are still not fully understood.

(4) Surface tensions and densities of substances related to atmospheric new particle formation were measured. These included ternary substances sulphuric acid + ammonia + water, and sulphuric acid + dimethylamine + water. Binary compounds, which consisted

of organic acids + water were also measured. The surface tensions of sulphuric acid + ammonia + water were found to be slightly lower than those used earlier in atmospheric model calculations by predictions from pure compound surface tensions. This implies that nucleation rates calculated with the new data would be slightly higher. The surface tensions of sulphuric acid + dimethylamine + water were found to be even lower than those of sulphuric acid + ammonia + water. If dimethylamine was present in similar quantities as ammonia in the atmosphere, this ternary system would be a very likely candidate to nucleate. The measured surface tensions and densities of organic acids + water are valuable input parameters for organic species in atmospheric models describing initial growth of particles as well as activation of atmospheric particles into cloud droplets.

(5) All measured surface tensions and densities were presented in a form of polynomial functions ready to be applied in atmospheric models. For sulphuric acid + dimethylamine + water the parameterization was restricted for the measured mole fraction range at 25 °C. For sulphuric acid + ammonia + water, the parameterization could be extrapolated to the whole mole fraction range at 25 °C. Thermodynamically consistent functions were fitted to the surface tensions and densities of organic acids + water. The fitted functions were extrapolated to cover the whole mole fraction range of an aqueous solution, at 25 °C for densities, and as a function of temperature for surface tensions.

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