Classical Nucleation Theory – Power Cycle Remarks

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Nucleation processes in binary gaseous water-based systems are investigated experimentally and numerically. The *Classical Nucleation Theory* (CNT) is modified to treat a special case of admixtures – electrolytes. Thermodynamic features of aqueous electrolytic solutions are described in a slightly different way from that for ordinary liquid mixtures. Namely, the excess Gibbs energy is expressed in terms of the osmotic coefficient and the mean stoichiometric activity coefficient instead of the activity coefficients. Moreover, the vapor–liquid equilibrium is characterized by the partitioning constant rather than by the saturation pressure of the admixture. The presented nucleation theory is utilized to numerically investigate the system of water and sodium chloride, which is considered to cause the early condensation in the Wilson zone of a steam turbine, and it is therefore of key importance in the power cycle industry.

1. Introduction

Nucleation processes in gases and liquids are of interest to many researchers nowadays. Thorough knowledge of nucleation processes is of high importance in various branches of industry (power cycles) or environmental science (atmospheric aerosol formation). The need to theoretically describe these processes resulted, after more than a century of investigations started by Gibbs [1] and Wilson [2], into the so-called Classical Nucleation Theory [3,4,5], which is based on the evaluation (in the capillary approximation) of the nucleation work. Calculations based on the CNT have been widely used as a complement to nucleation experiments. Unfortunately, the experimental results show some deviations from the predictions of the CNT. This was also shown by our calculations [6]. We have evaluated the nucleation properties, according to the CNT, for a wide set of binary water-based mixtures. Available experimental results of water–methanol [7] and water–sulfuric acid [8,9] show the differences of several orders of magnitude in the nucleation rate compared to our numerical results. Nevertheless, the range of temperatures and pressures where a nucleation process can occur is estimated quite accurately.

In this paper, we focus on systems with electrolytic admixtures. These systems require a few modifications of the CNT which are summarized in the next section. The theory will be used to investigate the nucleation of steam polluted with sodium chloride at elevated temperatures. This substance is considered to cause the early condensation in power cycles [10,11]. We will mention the adopted thermodynamic properties in sec.3, and the results of our numerical simulations are presented in sec.4.

2. Nucleation Theory

As mentioned above, the presented nucleation theory concerns gas-to-liquid homogeneous binary nucleation processes. Water, the prevailing component of the gaseous phase in our considerations, will be denoted by the subscript *1* in the following text. The other component of the binary gaseous mixture, indexed with *2*, is considered having a specific feature, being an electrolyte namely. In this special case, we can account for the chemical non-ideality of the liquid phase, or the newly formed droplet in other words, utilizing the osmotic coefficient ϕ and the mean stoichiometric activity coefficient $\gamma_{\pm}$ of the respective aqueous solutions.

The *capillary approximation*, the basic assumption of the CNT, allows us to describe the newly formed nucleus with the properties of the macroscopic liquid phase. In this sense, we consider the nucleus being spherical, having a

radius r, volume $V = \frac{4}{3}\pi r^3$, and surface $A = 4\pi r^2$. Its density ρ, surface tension σ, and chemical potentials of each component g_{li} match those of the corresponding macroscopic aqueous solution. We use these properties to evaluate the *nucleation work* W. The nucleation work, which accounts for the energy needed to create a particular nucleus, is evaluated as a free energy difference between a small system of a gaseous mixture surrounding the particular nucleus and the same gaseous system but without the nucleus. The general form of the nucleation work can be written as [12]

$$W = -V(p_l - p_g) + \sigma A + \sum_{i=1}^{2}(g_{li} - g_{gi})n_{li} \quad (1)$$

where the properties of the gaseous mother phase are denoted with the subscript g, and the properties of the liquid nucleus are indicated by the subscript l, p stands for pressure, and n_{il} are the numbers of molecules of the two respective components of the nucleus.

Let us focus on the electrolytic nature of our admixtures. Consider a general electrolyte $M_{v_+}X_{v_-}$ which dissociates into v_+ cationic species M, and v_- anionic species X according to the following scheme

$$M_{v_+}X_{v_-} \rightleftharpoons v_+M + v_-X \quad (2)$$
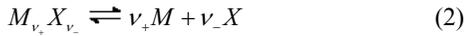
The suitable parameters of the resulting aqueous solution are the ion number $v = v_- + v_+$, and the mean stoichiometric molality $m_{\pm} = \sqrt[v]{m_+^{v_+}m_-^{v_-}}$. Now, we can express the chemical potential of a water molecule inside the nucleus as [13]

$$g_{l1} = g_{l1}^{\circ} - kT\phi M_1 v m_{l2} \quad (3)$$

where M_1 is the molecular weight of water, m_{l2} is the molality of the admixture in the nucleus, and the standard chemical potential g_{l1}° refers to the pure liquid water. The dissociated admixture is in our treatment characterized with the mean stoichiometric parameters. That is, although there are two distinct species in the solution, cationic and anionic, we describe them as a single one. The chemical potential of an admixture "molecule" inside the nucleus then reads

$$g_{l2} = g_{\pm}^{\circ} + vkT \ln \gamma_{\pm}m_{\pm} \quad (4)$$

where the standard chemical potential refers to the *1–molal* solution of the appropriate electrolytic species.

The chemical potential of a gas-phase component takes usually the general form $g_g = g_g^{\circ} + kT \ln a_g$, where the standard state g_g° lies on the saturation line of the pure component, and a_g is the corresponding activity. This description can be used for water quite comfortably, but our electrolytic admixtures are not the case. Mostly, there is no gas-liquid saturation line of the pure species in the range of temperatures and pressures we consider. We use another property that describes the gas–liquid equilibrium distribution of our admixture. The *partitioning constant* relates the activity of the admixture in the gaseous phase and the admixture activity in the aqueous solution in the following way

$$K_D = \frac{\gamma_{g2}m_{g2}}{(\gamma_{\pm}m_{\pm})^v} \quad (5)$$

Partitioning constants of many admixtures related to power cycles were evaluated by D. A. Palmer's group at the Oak Ridge National Laboratory. In principle, admixture molalities are measured in the liquid solution and in the gaseous mixture at vapor–liquid equilibrium. The experimental apparatus used for the measurements is described in the works of Palmer *et al.*[19,22,25]. The activity coefficients needed for the evaluation of the partitioning constant (5) were found in the literature, and in our calculations it is necessary to use exactly the same fits of the activity coefficients to account properly for the vapor–liquid equilibrium distribution of our admixtures.

The partitioning constant is usually expressed as a temperature-dependent function, but the temperature range of validity of the fit has to be considered. The volatilities of some admixtures may be very low, and then it is impossible to measure the molality of such an admixture in the gaseous phase at lower (atmospheric) temperatures. The experiments have to be conducted at elevated temperatures, and then the extrapolation to lower temperatures may be inaccurate.

With all the important properties of our system acquired, we arrive at the final nucleation work formula for the binary electrolytic nucleus

$$W = \sigma A + \tag{6}$$
$$+ kT n_{l1} \left(-\phi M_1 \nu m_{l2} - \ln\left(\frac{f_{g1}}{f_{g1}^{sat}} \right) - \ln a_{g1} \right) +$$
$$+ kT n_{l2} \left(\nu \ln(\gamma_{\pm} m_{\pm}) + \ln(K_D x_{g1} M_1) - \ln a_{g2} \right)$$

Here, the gas phase fugacities f_{g1}, f_{g1}^{sat} are usually approximated with pressures, and activities a_{gi} are idealized to molar fractions x_{gi}.

The extreme (saddle point) of the nucleation work surface $W(n_{l1}, n_{l2})$ determines a meta-stable state of the nucleus, and it is referred to as *critical state*. Due to the complexity of the expression (6), it is necessary to use numerical iterative methods to find the solution of the following equations

$$\frac{\partial W}{\partial n_1} = \frac{\partial W}{\partial n_2} = 0 \tag{7}$$

to obtain the critical composition (n_{l1}^*, n_{l2}^*), and the critical nucleation work W^*.

To describe the kinetics of the nucleation process we evaluate the *nucleation rate*. The nucleation rate accounts for the number of clusters which pass the critical size per second and per cubic meter. The general form of the nucleation rate is given as according to Trinkaus [5]

$$J = c_0 \frac{|\lambda|}{\sqrt{2\pi kT \det \mathbf{D}}} \exp\left(-\frac{W^*}{kT} \right) \tag{8}$$

Here, c_0 is the initial concentration of monomers (molecules of both species) in the gaseous phase, $\mathbf{D}$ is the matrix of second derivatives of W in the saddle point in coordinates rotated in the direction of the nucleation rate vector, and λ is the negative eigenvalue of $\mathbf{D}$.

3. Numerical Simulations

We have developed a computer program which utilizes the nucleation theory described in the previous section. The input parameters defining the thermodynamic state of the gaseous mixture are the total pressure, the temperature, and the molar

fractions of both components. This information is used to evaluate the nucleation work surface $W(n_{l1}, n_{l2})$. Afterwards, an iterative procedure is employed to find the saddle point of the nucleation work surface. As a result, several parameters of the nucleation process are calculated, e.g. critical cluster composition, critical cluster radius, critical nucleation work, and above all the nucleation rate.

When evaluating the nucleation work, additional thermodynamic properties of the species involved are required. The necessary properties can be found in the literature, either in the form of formulas fitted to the experimental data, or in the form of raw experimental data. In the second case, we have fitted the data to the following formula

$$\sigma = \frac{\sum_i (a_i + b_i T) x^i}{1 + \sum_j c_j x^j} \tag{9}$$

which was proven to fit the surface tension and density data of binary liquid mixtures quite well. The sources of experimental data and sources of fitted formulas are summarized in Table 1. Furthermore, the saturation pressure of pure water was fitted by Wagner and Pruss [14], and the fugacity coefficient of pure steam was evaluated by Harvey and Lemmon [15].

Table 1. The sources of thermodynamic properties of aqueous solutions. Links with asterisk refer to experimental data which were fitted to the equation (9).

Mixture property	H$_2$O with		
	NaCl	NaOH	HCl
Density	[16]	[20]*	[20]*
Surface tension	[17]*	[21]	[23]
MSA coefficient	[18]	[22]	[24]
Osmotic coefficient	[18]	[22]	[24]
Partitioning constant	[19]	[22]	[12]

4. Results and Discussion

We ran our calculations of the $H_2O - NaCl$ system at 200 ºC, which is applicable to some LP turbines [10]. The nucleation rate is evaluated as a function of the total pressure of the binary system and the molar fraction of the admixture.

The results of our calculations are rather surprising. The nucleation rate of steam seems not
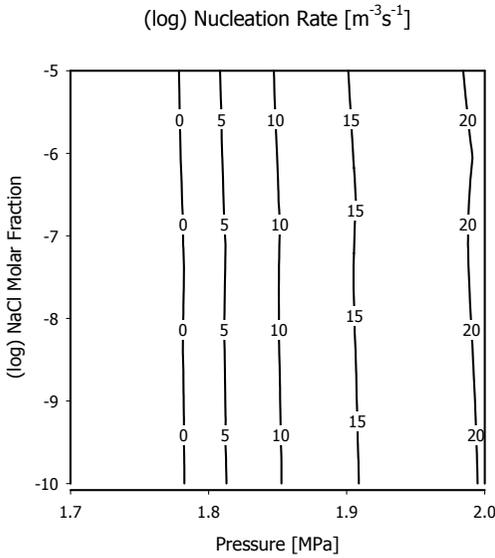
(log) Nucleation Rate [m^{-3}s^{-1}]

Fig. 1. The nucleation rate of the $H_2O - NaCl$ mixture at 200 ºC.

to be affected by the addition of sodium chloride. Fig.1 shows that the nucleation rate of the $H_2O - NaCl$ mixture is constant over the range of sodium chloride molar fractions spanning from 10^{-10} to 10^{-5}, and approximately equals the nucleation rate of pure steam.
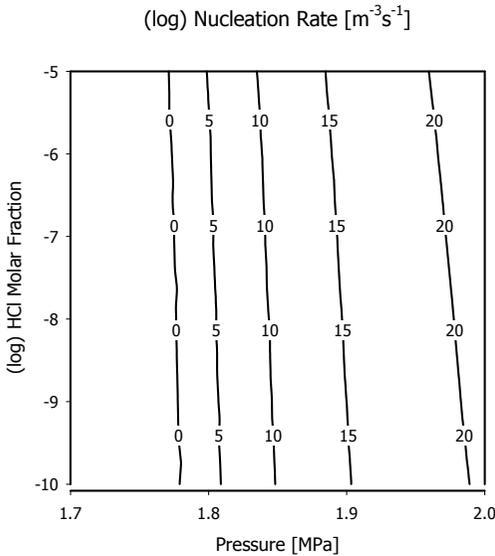
(log) Nucleation Rate [m^{-3}s^{-1}]

Fig. 2. The nucleation rate of the $H_2O - HCl$ mixture at 200 ºC.

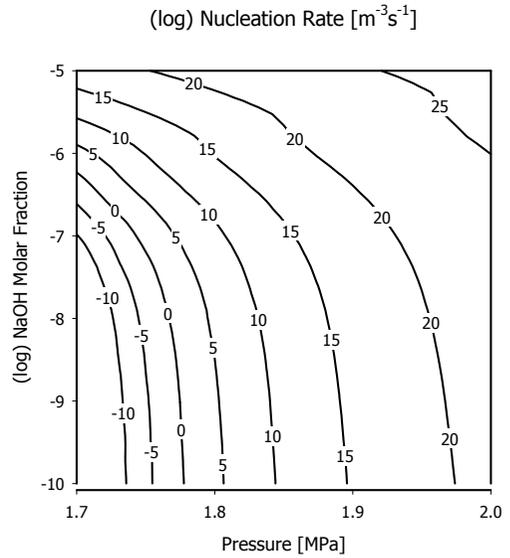(log) Nucleation Rate [m^{-3}s^{-1}]

Fig. 3. The nucleation rate of the $H_2O - NaOH$ mixture at 200 ºC.

We propose to solve this peculiar situation by considering the following chemical reaction taking place in the gaseous mixture
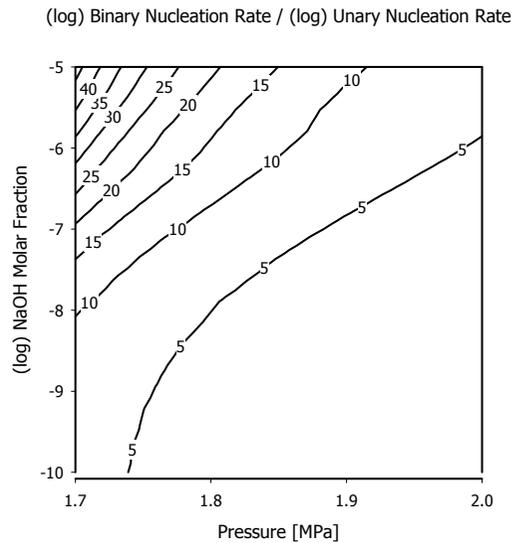
$$NaCl + H_2O \rightleftharpoons HCl + NaOH \qquad (10)$$

(log) Binary Nucleation Rate / (log) Unary Nucleation Rate

Fig. 4. The comparison of binary nucleation rate in the $H_2O - NaOH$ mixture and unary nucleation rate of pure H_2O at 200 ºC.

In other words, we suppose that exposing the $H_2O - NaCl$ gaseous mixture to the various mechanical stresses, elevated temperatures, and electrostatic forces, which apply during a power cycle, might cause some of the water molecules and sodium chloride molecules to break up and "accidentally" form the molecules of hydrochloric acid and sodium hydroxide. That is the reason we also investigate the nucleation processes in the $H_2O - HCl$ and the $H_2O - NaOH$ binary systems.

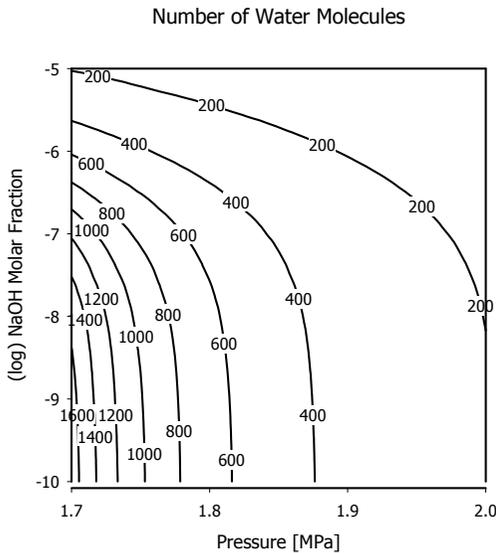The nucleation rate of steam polluted with

Number of Water Molecules

Fig. 5. The number of water molecules in the critical cluster in the $H_2O - NaOH$ nucleating mixture at 200 ºC.

hydrochloric acid shows the same behavior as was the case of sodium chloride. Figure 2 shows that adding hydrochloric acid to the pure water vapor does not influence the nucleation process considerably.

The admixture which is able to accelerate the nucleation process is, according to our calculations, the sodium hydroxide. We see (Fig. 3) a steep rise of the nucleation rate with increasing molar fraction of sodium hydroxide in the steam. The effect of adding sodium hydroxide to the steam can be observed in Fig. 4. Here, the nucleation rate of the binary $H_2O - NaOH$ mixture is compared to the unary pure-water nucleation rate. For example, at 1.7 MPa, the nucleation rate of steam with a 10^{-8} molar fraction of sodium hydroxide is 10^{10} times
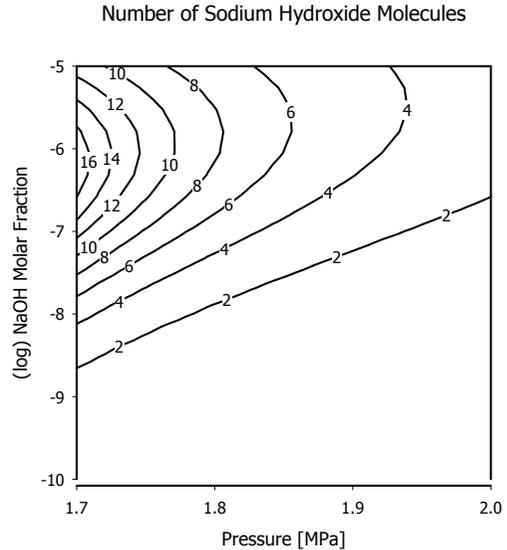
Number of Sodium Hydroxide Molecules

Fig. 6. The number of sodium hydroxide molecules in the critical cluster in the $H_2O - NaOH$ nucleating mixture at 200 ºC.

larger than the nucleation rate of pure water vapor at the same thermodynamic conditions. The composition of the critical cluster is shown in the Figs. 5 and 6. Although the final composition of the condensate is governed by the availability of both components in the surrounding mixture during the cluster growth, the critical cluster composition can give us a slight idea of the resulting condensate aggressiveness.

5. Conclusions

We have theoretically described the nucleation processes in binary mixtures that form electrolytic solutions by modifying the Classical Nucleation Theory. Utilizing this model, we have numerically investigated the nucleation processes in the $H_2O - NaCl$, the $H_2O - HCl$, and the $H_2O - NaOH$ binary mixtures at 200 ºC. Our results show that tiny fractions of sodium hydroxide are able to accelerate the nucleation of steam considerably. On the contrary, sodium chloride or hydrochloric acid do not affect the nucleation rate of the water vapor in any way. Nevertheless, the nozzle experiments [10], and the observations on operating turbines [11] can be explained by the chemical kinetics (10) as well.

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