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# The reverse Wilson chamber method as a tool for heterogeneous nucleation studies

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*Abstract*: On the basis of the Richarz–Powell equation the effect of different factors (temperature, the nature of carrier gas and condensing liquid etc.) has been investigated in detail. The simple theory of the RWC method proposed in this paper is generalized for the more complicated case of binary (multicomponent) heterogeneous nucleation.

The deviations from the adiabatic regime have also been discussed.

*Key words*: Condensation on substrate – reverse Wilson chamber – supersaturation – heterogeneous nucleation – Wilson cloud chamber

## Introduction

The reverse Wilson chamber (RWC) was proposed in 1981 [1] as a method for heterogeneous nucleation studies. The method has been applied to critical supersaturation measurements [2–5] as well as to the experimental investigation of the temperature dependence of critical supersaturation [6, 7].

In a most recent paper [8] a new version of the RWC method, suitable for direct observation of droplet growth on a liquid substrate and surface concentration of droplets (nuclei) determination has been proposed. This version has also been used in [7].

In [5] a detailed experimental investigation of the regime in RWC has been carried out. The results obtained show that the compression regime in the chamber is intermediate between adiabatic and isothermal.

But despite the many technical improvements made and important results obtained a complete theory of the method has not been developed until now. The aim of this paper is to present a simple theory of the RWC method in order to account for the factors that determine the supersaturation value. It is of extreme importance to know the exact value of the supersaturation, $\ln S$, since $\ln S$ is the main driving force of any nucleation process [9].

The effect of temperature, nature of the carrier (inert) gas and the vapor under investigation, degree of compression, etc. on the supersaturation is presented.

A generalization for the case of binary (multicomponent) heterogeneous nucleation is also given.

### *Physical background of RWC method*

Since the RWC method (experimental set-up, mode of operation etc.) is described in detail elsewhere [5], we shall recall here only the main features of the method with an emphasis on the basic physical principles, which lie in the root of the RWC method.

In many respects this method is a reverse version of the classical Wilson cloud chamber (also termed piston-cloud chamber or expansion cloud

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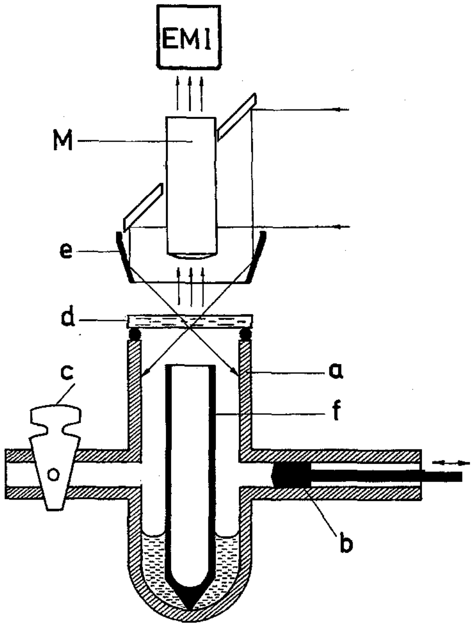

Fig. 1. A simplified version of the reverse Wilson chamber (RWC) given in [1]. M – light microscope; a – glass chamber; b – piston by which supersaturation is produced; c – tap; d – removable chamber lid (circular glass plate) the inner surface of which is covered with a thin layer of the liquid – substrate; e – objective of the light microscope *M*; f – nontransparent ("black" Pt. cylinder). More detailed description of the RWC is given in [5]

chamber). In the classical Wilson cloud chamber a given volume of an inert (noncondensing gas) gas saturated with the vapors of the liquid under investigation, is suddenly expanded.

Thus, the vapor–inert gas mixture is cooled and rapid condensation occurs in the bulk of chamber (homogeneous nucleation). In the same time, the chamber walls preserve for some time their initial temperature and no condensation takes place there.

In the RWC, the inert gas–vapor mixture is suddenly compressed to produce a heating of the mixture, but the chamber walls remain, of course, for a short time, at a temperature close (or even equal) to the initial one. In any case this temperature is lower than the temperature in the bulk of chamber. This temperature difference between the inert gas–vapor mixture inside the chamber and the chamber walls causes rapid condensation on the walls. If the removable top wall (circular glass plate) is covered on its inside surface with a layer of a liquid insoluble in the condensing liquid, heterogeneous nucleation on a liquid substrate may be observed [1–8]. The use of liquid substrates eliminates one of the usual objections against the solid ones, i.e., solids are in general geometrically and energetically nonhomogeneous which presupposes the existence of active sites. These sites can promote the nucleation process and, therefore, this facilitated nucleation leads to underestimation of the critical supersaturation and overestimation of the nucleation rate.

Nevertheless, the RWC method is appropriate for heterogeneous nucleation studies on solid substrates. In the latter case the top wall must be treated in such a way that sufficient smoothness of the inner surface is ensured.

Evidently, the classical Wilson cloud chamber method is suitable for homogeneous nucleation only, since in this case the chamber walls, which preserve their initial temperature, exhibit no possibility for condensation on them.

Therefore, the Wilson cloud chamber is a device only for homogeneous nucleation studies, while the reverse Wilson chamber method is a tool for heterogeneous nucleation investigations.

### *Supersaturation*

Let the system under consideration (RWC) be characterized by the pressure of carrier gas $P_g$, partial vapor pressure of the liquid under investigation $P_v$, total pressure of the vapor-carrier gas mixture $P_t$, and the temperature $T$. A scheme of the reverse Wilson chamber is presented in Fig. 1. We shall not give here a more detailed schematic, which is given in [5], since it is not necessary for the exposition that follows.

We shall estimate the supersaturation assuming that the compression of the inert gas-vapor mixture takes place as an adiabatic process. Although this assumption is incorrect it allows to render an account of the factors that may affect the supersaturation. However, the deviations from the adiabaticity must be taken into account in order to obtain the exact value of the supersaturation [5]. This problem will be discussed in the last section of the present paper.

Let the system under consideration undergo a change in state by an adiabatic process. If $P_i$, $V_i$, and $T_i$ are the partial vapor pressure, volume and temperature in the initial state (before compression is made) and $P_f$, $V_f$, and $T_f$ are the corresponding values of those quantities in the final state (after compression), and one can use the Poisson adiabatic equation $PV^{\gamma} = \text{const}$ to obtain the supersaturation value [1]:

$$S = \left[1 + \frac{\Delta V}{V}\right]^{\gamma} \tag{1}$$

or

$$\ln S = \ln\left[1 + \frac{\Delta V}{V}\right]^{\gamma} . \tag{2}$$

In Eqs. (1) and (2) it is supposed that $V_i = V_f + \Delta V$, and $\gamma = C_p/C_v$ ($C_p$ and $C_v$ are the constant-pressure and constant-volume heat capacities, respectively). $\Delta V$ is the volume change due to compression.

In 1906 Richarz [10] derived an expression which relates $P_g$, $P_v$, $P_t$, and $\gamma$:

$$\frac{1}{\gamma - 1} = \frac{1}{\gamma_g - 1}\frac{P_g}{P_t} + \frac{1}{\gamma_v - 1}\frac{P_v}{P_t} . \tag{3}$$

In this equation $P_t$ (for perfect gases $P_t = P_g + P_v$) is the total pressure of the carrier gas-vapor mixture; $\gamma_g$ and $\gamma_v$ being the $C_p/C_v$ ratios of the inert gas and vapor, respectively.

Equation (3) was rederived in 1928 by Powell [11] and is referred to in the literature as the Richarz or Powell equation. It should be noted that this equation is often used in Wilson cloud chamber studies performed at increased total pressure [12].

Equation (3) can easily be generalized for the case when, in the vapor phase, $n$ condensing species and just one carrier gas are presented.

In this case Eq. (3) is to be rewritten as follows

$$\frac{1}{\gamma - 1} = \frac{1}{\gamma_g - 1}\frac{P_g}{P_t} + \sum_{i=1}^{n} \frac{1}{\bar{\gamma}_{vi} - 1}\frac{P_{ri}}{P_t} . \tag{3a}$$

In the above equation $\gamma_{vi}$ is the $C_p/C_v$ ratio of the $i$th component and $P_{vi}$ its partial pressure.

For perfect gases

$$P_t = P_g + \sum_{i=1}^{n} P_{vi} .$$

## Factors that govern the supersaturation level in RWC

### *a) Dependence of the supersaturation on the nature of carrier gas and condensing liquid*

Since $\gamma = C_p/C_v$ is different for different carrier gases, the supersaturation under fixed $\Delta V/V$ and $T$ will also differ. For example, $\gamma = 1.66$ for Ar-water vapor mixture and 1.40 for air-water vapor [12]. Therefore, if one produces one and the same degree of compression $\Delta V/V$, the supersaturation will be higher in Ar atmosphere than in air atmosphere, which follows immediately from Eqs. (1) and (2). On the other hand, $\gamma$ is dependent on $\gamma_v$, so if one condenses $C_2H_5OH$ instead of $H_2O$ in an air atmosphere, the supersaturation in the former case will be lower under the same conditions (temperature, $\Delta V/V$, and $P_t$). Therefore, a larger compression is needed in order to produce the same supersaturation.

### *b) Dependence of the supersaturation on the inert (carrier) gas partial pressure*

It follows from Eq. (3) that a decrease in the total pressure $P_t$ will cause an increase in the $P_v/P_t$ ratio. At the same time, the ratio $P_g/P_t$ remains practically constant, because in the typical cases $P_g \gg P_v$. This is the reason $\gamma$ will decrease and, therefore, at $\Delta V/V = \text{const}$, the supersaturation will also be decreased.

In contrast, if one increases $P_g$, the same supersaturation level will be reached at lower degree of compression. For instance, $\gamma = 1.354$ at $P_t = 6$ mm Hg, while at $P_t = 1140$ mm Hg $\gamma = 1.400$; in both cases the system under investigation is water vapor–air.

This effect is even more pronounced in the case of the air–ethanol system. For this carrier gas-vapor mixture, $\gamma = 1.396$ at $P_t = 1140$ mm Hg and $\gamma = 1.125$ at $P_t = 6$ mm Hg.

The effect of increased total pressure is often used in the case of nucleation on charged particles (ions, elementary particles), because the increase in $P_t$ (due to $P_g$ increase) allows more clear tracks to be obtained [12].

### *c) Dependence of the supersaturation on the degree of compression and the initial temperature*

It is clear from Eqs. (1) and (2) that the supersaturation produced will be higher at higher $\Delta V/V$ values, if $\gamma$, $T$, and $P_t$ are kept constant. For example, at $\Delta V/V = 0.15$, $\ln S = 0.196$, while at $\Delta V/V = 0.3$ the supersaturation $\ln S$ will be equal to 0.367. In both cases the system under investigation is air–water vapor.

Increasing the initial temperature at $V = \text{const}$ and $P_t = \text{const}$, the ratio $P_v/P_t$ increases more rapidly than $P_g/P_t$ ratio, and therefore, $\gamma$ must decrease as follows immediately from Eq. (2).

Consequently, if one wants to produce a given supersaturation level (respectively temperature difference between gas phase and the substrate) at two different temperatures, a higher degree of compression ($\Delta V/V$) is needed at the higher temperature.

### *d) Binary heterogeneous nucleation*

Binary or (heteromolecular) nucleation takes place when the supersaturated vapors consist of a mixture of the condensable species 1 and 2 out of which clusters of a given composition are formed. Evidently, in this case the partial pressures of the components 1 and 2, $P_{v1}$ and $P_{v2}$ are strongly dependent on the composition of the liquid mixture. According to the well-known Duhem–Margules equation [13], the partial pressures of two components $P_{v1}$ and $P_{v2}$, respectively, follow the relation

$$\frac{d\ln P_{v1}}{d\ln P_{v2}} = -\frac{1-X}{X}, \tag{4}$$

where $X$ and $1 - X$ are the corresponding mole fractions.

Equation (4) can easily be solved by making use of the procedure first proposed by Lewis and Murphee [14] if the total vapor pressure at given composition is known.

### *e) Deviation from the adiabaticity*

As was pointed out at the beginning of the present paper, the compression regime in RWC is not strictly adiabatic but is intermediate between adiabatic and isothermal depending upon the time of compression $\tau$. The calibration curves given in [5] presented in coordinates $1 + \Delta P/P$ vs. $1 + \Delta V/V$ allow us to recognize the deviations from the adiabatic regime in RWC [5].

The shorter the compression time the closer the adiabatic is to a straight line $1 + \Delta P/P$ vs. $1 + \Delta V/V$. At compression times $\tau \geq 0.4$ s the regime in the chamber is an isothermal ($PV = \text{const}$) and no detectable condensation can be observed [15].

Unfortunately, adiabatic regime in a reasonable time of compression cannot be realized.

In any case, the calibration procedure described in [5] is obligatory in all cases in order to obtain the exact value of the supersaturation applied.

Therefore, Eqs. (1) and (2) must be rewritten in the following form

$$S = \left[1 + \frac{\Delta V}{V}\right]^{\gamma_{\text{eff}}} \tag{1a}$$

$$\ln S = \ln\left[1 + \frac{\Delta V}{V}\right]^{\gamma_{\text{eff}}}, \tag{2a}$$

where $\gamma_{\text{eff}} = f(\tau)$ and, evedently,

$$1 < \gamma_{\text{eff}} < \gamma = \frac{C_p}{C_v}. \tag{5}$$

This means that the real regime in the chamber can be described as a polytropic process following the well-known equation

$$pV^k = \text{const},$$

where $k$ ranges from large negative to large positive values, and where $k$ is an empirically determinable parameter. It is clear that in our case $k = \gamma_{\text{eff}}$.

## Conclusions

It was established in the present study that several factors (temperature, degree of compression, nature of the inert and condensing gases, etc.) influence the supersaturation level in RWC. Since the regime in the chamber is not adiabatic but is intermediate between adiabatic and isothermal, the use of the calibration curves reported in [5] is obligatory in order to obtain the exact value of $\ln S$ which is the main driving force of the heterogeneous nucleation process because the nucleation rate $J$ strongly depends on $\ln S$ through the well-known Volmer equation [16].

Nevertheless, the Richarz–Powell equation allows us to predict direction of changes in the supersaturation, when changing the above mentioned factors that govern the supersaturation level.

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