

# Ice Clouds: Atmospheric Ice Nucleation Concept versus the Physical Chemistry of Freezing Atmospheric Drops

In this viewpoint, we show that the Atmospheric Ice Nucleation Concept (AINC), which is prevalent in the atmospheric scientific community dealing with the formation and modeling of ice clouds, is scientifically invalid and misleading. We also show that instead of the AINC one has to consider the genuine physical chemistry of freezing supercooled atmospheric drops. Being globally widespread, ice clouds are important climate regulators. Ice clouds, especially upper tropospheric (UT) cirrus clouds, which cover approximately 30% of the Earth's surface with a larger frequency of occurrence in the tropics,<sup>1</sup> redistribute water vapor (a dominant greenhouse gas) to lower altitudes, reflect shortwave solar radiation, trap long-wave terrestrial radiation,<sup>2</sup> and supply surfaces for heterogeneous reactions destroying UT ozone<sup>3</sup> (an important greenhouse gas at high altitudes). In winter/spring polar stratosphere, ice polar stratospheric clouds (type II ice PSCs) play a crucial role in the formation of ozone holes.<sup>4,5</sup> Because of their important role in the Earth's climate, understanding the formation, development, and the physical and chemical properties of ice clouds is of paramount importance.

**AINC.** In the atmosphere, liquid drops practically never exist as pure water drops but contain different soluble and insoluble organic and inorganic materials. Here we will consider only soluble materials. The concentration and number of solutes in atmospheric drops varies within large limits. For example, in the UT and low stratosphere, aqueous drops can contain as much as 25–30 wt % H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.<sup>6–8</sup> There are works reporting that UT aqueous drops may contain more than 50 wt % sulfate/organic mixture.<sup>9</sup> Ice PSCs and a large fraction of UT cirrus form *in situ* due to the freezing of supercooled aqueous drops.<sup>6–9</sup> It is important to understand what is going on with solutes during freezing and how they affect the growth and physical and chemical properties of ice particles. Unfortunately, over the past several decades, atmospheric scientists dealing with ice clouds have ignored the fate of solutes during the formation of ice clouds. A reason for this is that they do not consider the entire freezing process but focus only on ice nucleation.<sup>10</sup> However, ice nucleation is only an initial stage of one indivisible freezing process that consists of an ice nucleation event and subsequent fast ice growth. Further, atmospheric scientists equate ice nucleation with freezing<sup>11,12</sup> and presume that this “ice-nucleation/freezing” event produces faceted pure ice crystals (Figure 1). A lot of literature<sup>11–15</sup> and numerous conferences<sup>16</sup> and workshops<sup>17</sup> have been dedicated to atmospheric ice nucleation. We name this approach to the study of ice clouds the atmospheric ice nucleation concept, AINC.

**Physical Chemistry of Freezing Supercooled Aqueous Drops.** Ice is highly intolerant to impurities because the ice lattice is built up by strong and directional hydrogen bonding between H<sub>2</sub>O molecules.<sup>18</sup> Since the size and charge of solute molecules and ions differ from those of water, they are effectively expelled from the ice lattice during ice crystallization. Thus, freeze-induced phase separation (FIPS) into pure ice

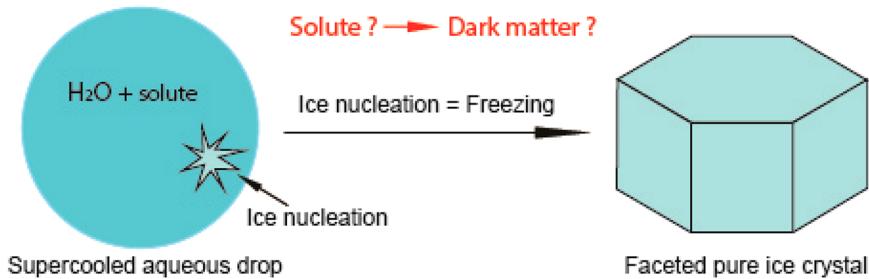
and a freeze-concentrated solution (FCS) occurs during the freezing of aqueous solutions.<sup>19,20</sup> FIPS occurs also during freezing upon warming of glassy solutions.<sup>21</sup> In the UT and low stratosphere, where the amount of solutes in aqueous drops is large, FIPS leads to the formation of mixed-phased particles: an ice core enveloped with a FCS coating<sup>7,8,22</sup> (steps 1–3 presented in Figure 2). Consequently, independently of whether hexagonal ice I<sub>h</sub>,<sup>23</sup> cubic ice I<sub>c</sub>,<sup>13</sup> disordered stacking ice with a random distribution of cubic and hexagonal layers<sup>15,24</sup> or other ices nucleate within aqueous drops, the ice particles formed will be coated with a FCS. This FCS coating determines the surface reactivity, radiative properties, and water vapor uptake at the beginning of ice cloud development.<sup>6–8,25</sup> FIPS occurs independently of whether the freezing of aqueous solutions and atmospheric drops is triggered by homogeneous<sup>6–8</sup> or heterogeneous<sup>26</sup> ice nucleation. The existence of mixed-phase particles accounts for the elevated moisture often observed outside and inside upper tropospheric ice cirrus.<sup>6</sup>

Further, faceted ice crystals start forming by vapor deposition after a growing ice core has disrupted a diluted<sup>7</sup> FCS coating (step 4 in Figure 2). With time, ice grows and the diluted FCS coating will only partly cover ice crystals. In this case, surface reactivity will approach that of pure ice. Since the disruption of FCS coating on different mixed-phase particles is not simultaneous, those ice crystals, which first started to grow by vapor deposition, will have larger dimensions. The disrupted FCS coating may influence the geometry and aggregation of ice crystals. The concentration, geometries, aggregation and size spectra of ice crystals are main microphysical characteristics that govern the radiative properties of fully developed ice clouds. In the case of freezing less concentrated or diluted tropospheric drops, a FCS coating will be thinner or only partly cover an ice core. Here, step 4 in Figure 2 will start faster or even right after the freezing of the drops. In this case, microphysical characteristics of ice clouds will most probably differ from those of ice clouds developed from mixed-phase particles.

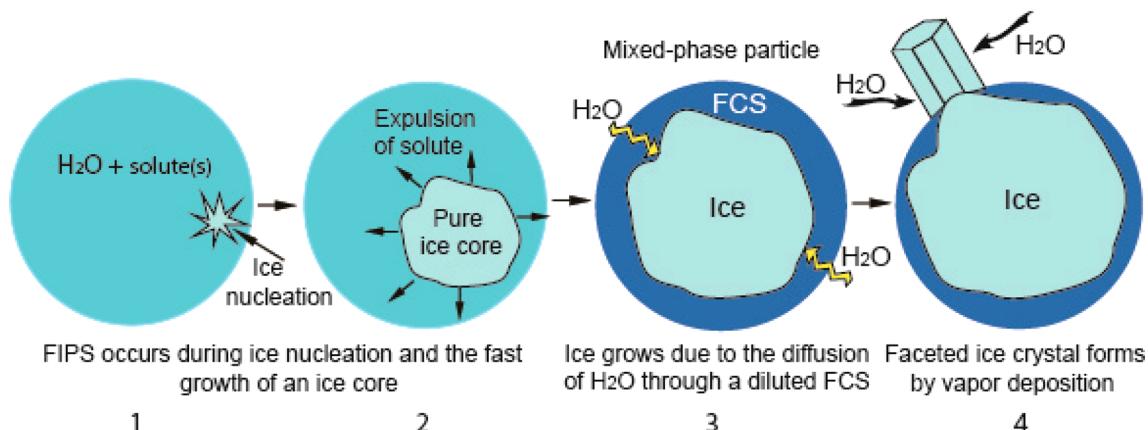
The visualization of FIPS during freezing and the ice/FCS morphology of frozen aqueous solutions can be viewed in videos recorded *in situ* during the freezing of aqueous solutions.<sup>20,22,27</sup> The images of mixed-phased particles formed during the freezing of micrometer-scaled drops relevant for the atmosphere are presented elsewhere.<sup>22,23</sup> Here, in Figure 3, we present for the first time images that demonstrate how faceted ice crystals form by vapor deposition on ice spikes after they have disrupted a FCS coating. These images confirm that in the atmosphere, the mechanism schematically depicted in step 4 in Figure 2 is indeed possible.

FIPS during freezing is a well-known phenomenon in medicine, biology, cryobiology, food industry, pharmaceutics, biotechnology, tissue engineering, etc.<sup>20,27,28</sup> More than

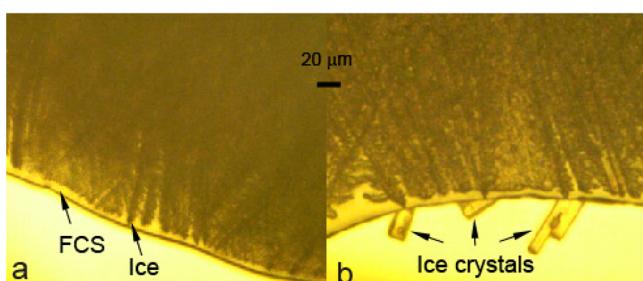
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**Figure 1.** Schematic representation of the formation of faceted ice crystal according to the AINC. The AINC does not consider the fate of solute(s), equates ice nucleation with freezing, and assumes the formation of faceted pure ice crystals. However, the vanishing of solutes during the formation of ice crystals violates the law of conservation of mass.



**Figure 2.** Schematic representation of the formation of a mixed-phase particle during the freezing of a supercooled atmospheric drop (steps 1–3). A pure ice core grows due to the diffusion of water molecules through a diluted FCS.<sup>7</sup> A faceted ice crystal starts forming by vapor deposition after a growing ice core has disrupted the diluted FCS (step 4).



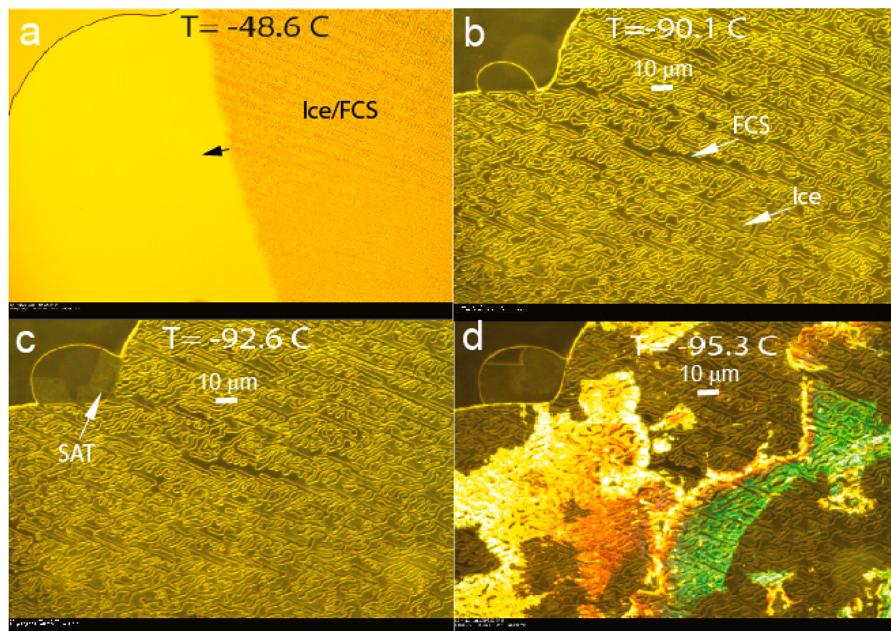
**Figure 3.** Optical cryo-microscopy (OC-M) images demonstrating the formation of faceted ice crystals by vapor deposition on ice spikes that have disrupted a FCS. (a) was taken right after freezing, (b) was taken some time after freezing. Note that the left ice crystal contains an air bubble. The images were taken from a frozen solution containing 25 wt % sucrose. The details of this freezing experiment are given in ref 20.

ten years ago, we suggested that FIPS also occurs during the freezing of atmospheric aqueous drops<sup>29</sup> and produces mixed-phase particles.<sup>6–8</sup> Our subsequent works and videos recorded *in situ* confirmed this suggestion. Currently, only our works disseminate experimental and visual results, which demonstrate that understanding the physical chemistry of freezing supercooled aqueous drops is crucial to move the study of ice clouds forward. Unfortunately, the atmospheric scientific community dealing with ice clouds keeps ignoring this stance.

**Origin of the AINC.** The currently prevalent AINC may have its origin in past freezing experiments on supercooled micrometer-scaled pure water drops. Such drops freeze

practically instantly (see videos in ref 22). This rapid freezing process could be a reason that in literature dealing with ice clouds, ice nucleation is commonly equated with freezing. For example, the terms of “homogeneous/heterogeneous ice nucleation” and “homogeneous/heterogeneous freezing” are interchangeable.<sup>11–14</sup> In the case of small pure water drops, equating ice nucleation with freezing may make sense, if the enthalpy of fusion evolved during freezing and the shapes of frozen drops are not taken into account. The freezing of micrometer-scaled water drops does not produce faceted ice crystals, as the AINC assumes.<sup>22</sup> The shape of frozen water drops is practically the same as that of liquid ones (see videos and images in ref 22). However, transferring the equation of ice nucleation with freezing to aqueous drops leads to the loss of important physical information, namely, FIPS into pure ice and a FCS. Below, we will critically examine the AINC and some unphysical situations that arise directly from it.

**Ice Nucleation Terminology of AINC.** That the AINC ignores the fate of solutes is best illustrated by ice nucleation terminology offered in ref 12. Reference 12 also aims to convey the offered ice nucleation terminology as general, and not only applicable to atmospheric ice nucleation. Terms such as “embryo or germ”, “embryo size”, “critical embryo size”, etc. are offered for the description of “ice nucleation in the atmosphere, in biological systems, and in other areas”. However, although in nature, including the atmosphere, water practically never exists in a pure state but as a component of various aqueous solutions, these terms are defined for ice nucleation in pure water only. Of course, in this case the terminology offered does not lead to confusion because ice is the only solid that forms in



**Figure 4.** OC-M images demonstrating the formation of three solids upon cooling of 27 wt %  $\text{H}_2\text{SO}_4$  solution. (a) An ice/FCS front moves from right to left. (b) The onset of  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (SAT) crystallization is seen as the formation of a FCS bubble. (c) The crystallization of SAT is seen in the FCS bubble. (d) The crystallization of  $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (SAO) (see a separate legend for SV). The details of this freezing experiment are given in ref 22.

pure water. In aqueous solutions, however, also other solids can nucleate and crystallize (see video 8 in ref 22). In Figure 4, we present images extracted from our *Supplementary Video* that demonstrate the formation of three solids upon cooling of 27 wt %  $\text{H}_2\text{SO}_4$  solution: ice, sulfuric acid tetrahydrate  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (SAT), and sulfuric acid octahydrate  $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (SAO). Earlier we reported that these solids form in the atmosphere during the freezing of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  drops.<sup>29</sup> Thus, in the case of aqueous solutions, the ice nucleation terminology offered in ref 12 leads to confusion, as it is not clear which nucleation process and of which solids is described.

Furthermore, in ref 12, in order to show that the offered ice nucleation terminology is general, the term “sample units” is used. The sample units, besides pure water drops, can also be “vials, test tubes, larvae, grains, ...”<sup>30</sup>. For such sample units, the terms “freezing rate” and “fraction frozen” are defined as the number of sample units that freeze per unit time and the fraction of frozen sample units, respectively. Note that the definition is based on the equation of ice nucleation with the complete freezing of sample units. In the case of pure water drops, the terms “freezing rate” and “fraction frozen” could partly be sensible as water drops do not freeze simultaneously (see videos in ref 22). However, in the case of aqueous drops, they overlook FIPS. In the case of concentrated solutions, these terms will not work at all, because even after multiple ice nucleation events, the concentrated solutions do not freeze but transform to glass (see Figure 8 in ref 22). In biology and cryobiology, they are even more irrelevant, as the emphasis is on the prevention of inter- and extracellular ice growth—not the number of larvae frozen per unit time. Thus, the ice nucleation terminology of AINC offered in ref 12 is misleading for those who work with freezing aqueous solutions in the atmosphere, pharmaceuticals, biotechnology, etc.

An alternative terminology should mirror the physical chemistry processes that occur during the freezing of supercooled atmospheric drops. For example, terms such as “ice embryo”,

“hydrate embryo”, “critical ice/hydrate embryo”, etc. could be applied. With regard to the term “freezing rate” in the case of pure water, one can view freezing rate as the pace of the rearrangement of  $\text{H}_2\text{O}$  molecules from liquid to solid/ice state. In aqueous solutions, this rearrangement is slower than that in pure water because of FIPS, which reduces the rate of freezing. The freezing rate may be estimated as the pace of the enthalpy of fusion evolved per unit time ( $\text{W}/(\text{g}\cdot\text{s})$ ) and/or per K ( $\text{W}/(\text{g}\cdot\text{K})$ ).<sup>22</sup> The freezing rate slows down with increasing concentration and the complexity of molecular structure of solute(s) due to increasing viscosity. At some concentration, the freezing process is completely terminated by glass transition at  $T_g$ .

**Ice Nucleation and Phase Diagram.** There are misconceptions of phase diagrams and their role in the interpretation of ice nucleation. For example, in the first two drafts of ref 12, a phase diagram was defined by “existing vapor pressure” and “existing water vapor pressure”.<sup>30</sup> Further, ref 12 reports that “Dissolved substances in water change the equilibrium phase boundaries and influence ice nucleation”. At constant atmospheric pressure, the phase boundary in the phase diagram of water is the equilibrium melting point of ice  $T_m = 273.15 \text{ K}$ . If a substance is dissolved in water, then we obtain a binary system whose phases are determined by, in addition to pressure and temperature, composition. In the range of compositions up to the first eutectic point, a binary phase diagram represents the line of equilibrium of the melting points of ice. Thus, “dissolved substances in water” do not “change the equilibrium phase boundaries” but produce new systems, which are described by a phase diagram with a larger number of variables. Since ice nucleation is a stochastic nonequilibrium process, which usually occurs at temperatures much colder than the equilibrium line of ice melting points, a phase diagram cannot be used for the interpretation of ice nucleation.

**Ice Nucleation Rate.** The AINC cannot account for what is going on with solutes during the “ice-nucleation/freezing” of

aqueous drops (Figure 1). This could be why a large fraction of AINC publications deal with ice nucleation in pure water drops.<sup>12,14,15,31</sup> Furthermore, it is thought that accurate weather and climate forecasts depend on the reliable predictions of ice nucleation rates in water.<sup>15</sup> However, this is not the case. First, as we mentioned above, pure water drops practically do not exist in the atmosphere. Second, even in the case of water drops, predicting the ice nucleation rate only gives an approximate ice crystal concentration in clouds. The radiative properties of fully developed ice clouds are determined, besides ice crystal concentration, also by the size distribution, geometries, and aggregation of ice crystals. These microphysical characteristics cannot be inferred from ice nucleation rate because freezing water drops do not produce faceted ice crystals (see videos in ref 22). The faceted ice crystals form by vapor deposition on frozen drops.<sup>22</sup> Thus, the ice nucleation rate in pure water has little to do with the radiative properties of ice clouds and, consequently, with weather and climate forecasts.

**Classical Nucleation Theory (CNT).** In the frame of the AINC, the CNT is a main tool for the calculation of ice nucleation rate. In the CNT, a macroscopic thermodynamic parameter such as surface tension is key. It enters in the power three exponential in the formula for calculation of the free energy of the formation of the critical embryo of a new phase. The capillarity approximation of the CNT assumes that (i) a nucleated embryo of a new phase possesses a macroscopic planar surface tension and (ii) the surface tension is independent of the size of the embryo.<sup>32</sup> The capillarity approximation assumes that there is a limit for the use of the CNT. For example, the CNT describes the nucleation of clusters consisting of 8–50 water molecules well but fails to describe the nucleation of smaller clusters.<sup>33</sup> However, within the frame of the AINC, the capillarity approximation is sometimes extended to embryos consisting of two (dimer ( $\text{H}_2\text{O}$ )<sub>2</sub>) or even of a single  $\text{H}_2\text{O}$  molecule.<sup>34</sup> Besides it being unphysical to refer to the phase state and surface tension of embryos consisting of two and one  $\text{H}_2\text{O}$  molecule, the unlimited use of the CNT further leads to other unphysical results. For example, the Gibbs free energy formation of an  $\text{H}_2\text{O}$  monomer is nonzero.<sup>34</sup> This nonzero Gibbs free energy formation of the  $\text{H}_2\text{O}$  monomer is then subtracted from the nucleation barrier of larger embryos. After the subtraction, the Gibbs free energy formation of a dimer ( $\text{H}_2\text{O}$ )<sub>2</sub> is  $\sim 0.8 \times 10^{-20}$  J for amorphous solid water (ASW) and  $1.8 \times 10^{-20}$  J for hexagonal ice (see Figure 1 in ref 34). Thus, a hydrogen bond between two  $\text{H}_2\text{O}$  molecules is not determined by electrostatic attraction, but depends on whether the authors of ref 34 interpret ( $\text{H}_2\text{O}$ )<sub>2</sub> as ASW or hexagonal ice. For comparison, the *ab initio* molecular orbital calculations on the binding energy of ( $\text{H}_2\text{O}$ )<sub>2</sub> is  $5.0 \pm 0.1$  kcal/mol<sup>35</sup> or  $\sim 3.5 \times 10^{-20}$  J, i.e., much larger than those reported in ref 34.

In macroscopic thermodynamics, a real interface between two phases is substituted by the Gibbs' surface model in which surface tension is attributed to a geometrical surface called the *surface of tension*.<sup>32</sup> Some time ago Tolman showed that the surface tension of small liquid drops decreases with increasing curvature.<sup>36</sup> Similarly, the surface tension of an ice embryo formed in the vapor phase and liquid water decreases with increasing curvature.<sup>32</sup> The capillarity approximation cannot be extended to embryos consisting of only several molecules, let alone dimers and monomers, where the concepts of macroscopic thermodynamics do not work.

**Water Activity Criterion (WAC).** Within the frame of the AINC, the WAC has been proposed in order to simplify the simulation of the formation of ice particles during the modeling of ice clouds.<sup>11</sup> The authors of ref 11 write "... we may compute the formation of atmospheric ice cloud particles through homogeneous nucleation as a function of temperature, aerosol size, and water activity without knowing the composition of the aerosols." This sentence clearly states that ice particles form through homogeneous ice nucleation and solutes are not considered. Further, the WAC also states that there exists a *homogeneous ice nucleation threshold* for ice supersaturation  $S_i$  above which atmospheric aqueous drops cannot exist in the liquid state but only as ice particles. The WAC is widely used in ice cloud modeling. In our earlier work,<sup>7</sup> we showed that multicomponent aqueous drops of size and composition relevant for the atmosphere could freeze at  $S_i$  noticeably higher than that predicted by the WAC. We also showed that the freezing of multicomponent drops produced mixed-phase particles.<sup>7</sup> Another publication also reported that binary aqueous drops freeze at  $S_i$  higher than the homogeneous ice nucleation threshold.<sup>37</sup> Unfortunately, reports of findings not adherent to the AINC are, to a large extent, ignored.

Overall, because of the substantial and basic conceptual errors of reasoning, the AINC is scientifically invalid and its ice nucleation terminology is misleading for those working with freezing aqueous solutions in the atmosphere, as well as in other fields of science and technology where freezing phenomena play an important role. It is unclear why atmospheric scientists dealing with ice clouds keep ignoring the genuine physical chemistry of freezing supercooled atmospheric drops. We do not speculate as to the reasons for ignoring works dealing with the FIPS in the atmosphere and reporting viewpoints on the formation of ice clouds different from that of the AINC. We merely wish to point out that the failure to consider the physical chemistry of freezing supercooled atmospheric drops will lead to a persisting stagnation in the study of the formation and modeling of ice clouds and their influence on climate.<sup>10</sup> This in turn will result in further waste of human resources, time, and money which, otherwise, could be redirected toward resolving the pressing phenomenon of climate change.

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## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b07926.

Description of video (PDF)

Video of triple freezing/crystallization of 27 wt %  $\text{H}_2\text{SO}_4$  solution (MPG)

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### Notes

The author declares no competing financial interest.

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