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Are All Types of Sublimation Equivalent?

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Abstract: The process of sublimation is defined unequally in various chemistry sources. Its standard definition is, in a way, analogous to that for evaporation. However, there is no special term for the sublimation equivalent to boiling! Being so, one should perhaps not be surprised that a number of misconceptions related to sublimation, (especially sublimation of iodine) exist. Here we make an attempt to explain the desirability of introducing a new term such as *bolimation*, for the special type of sublimation that is analogous to boiling, and hope it might help fighting the old and persistent misconception about iodine only subliming but not melting at atmospheric pressure.

Introduction

Definition of Sublimation. The IUPAC terminology compendium [1] defines sublimation as "the direct transition of a solid to a vapor without passing through a liquid phase. Example: The transition of solid CO_2 to CO_2 vapor". The microscopic meaning of the above definition is simply passing of molecules from a solid substance into the gaseous state of that substance. In this way, sublimation appears to be completely analogous to evaporation – passing of molecules from the liquid state/phase of the substance into its gaseous state.

As already mentioned elsewhere [2] if such a definition is adopted, it would be applicable to any substance in the solid state, at any pressure and any temperature above absolute zero. In the light of what has been said above, sublimation appears to be something rather trivial (at least, in the educational process), since, in principle, any solid substance at any temperature above the absolute zero – sublimes.

In reality, things are more complicated. When talking about sublimation, many people think of a process in which a solid, upon heating (at atmospheric pressure), transforms directly into gas, without being liquefied first [2]. This (the bolded text in the previous sentence) would be a more rigid definition of sublimation, and for many purposes it would be more useful. However, having in the same time the 'official definition' [1] as well as this ('more rigid') one [2], it is probably not surprising that on the issue of sublimation misconceptions exist for quite some time.

Misconception

Does Molten Iodine Exist at Atmospheric Pressure? When examples of subliming substances are given, the most usually quoted ones are dry ice (solid carbon dioxide), iodine and naphthalene [2–4]. Of course, in the light of the official definition of sublimation, all these substances can sublime, as well as many hundreds of others that are not mentioned. However, it is not true that upon heating at atmospheric pressure (≈ 1 bar) all these solid substances would transform into a gas without being liquefied! In fact, both iodine and naphthalene would first melt (at ≈ 114 °C and at ≈ 80 °C, respectively). The existence of liquid naphthalene and liquid iodine [5] is simply a fact. Yet, many people apparently have a distorted version of the reality and believe that 'liquid iodine does not exist' [6, 7]. This is clearly a misconception [8], but this misconception is present in the literature and in people's minds for quite a long time. The question is why?

Bolimation

Sublimation Analogous to Boiling. One of the possible reasons for the above widespread misconception is that we obviously lack a term for the sublimation process that is analogous to boiling. This is why we now try to coin it as bolimation = boiling + sublimation and define it as follows:

> Bolimation is a particular type of sublimation where a solid (substance) transforms into a gas, the partial pressure of which is equal to the external pressure (usually atmospheric pressure close to 1 bar).

Let us now briefly discuss the advantage of using the offered term.

Bolimation, as defined, is equivalent to the rigid definition of sublimation [2]. However, there are certain advantages to have a one-to-one correspondence between the terms for the two pairs of transitions: evaporation–boiling and sublimation–bolimation. All solid substances, as mentioned in the beginning, sublime. However, of the three mentioned (carbon dioxide, iodine, naphthalene) only carbon dioxide bolimes, while the other two (iodine and naphthalene) first melt and then boil.

We strongly believe that, if this clear-cut distinction had been made earlier (when the terminology of physical chemistry was being built), the number of misconceptions would have been severely reduced, in both the literature and the process of teaching/learning about phase transitions. We therefore appeal

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to the chemistry community to consider the importance and necessity for introducing bolimation (or some other, better coined term) for the process of sublimation that is analogous to boiling.

References and Notes

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