Answer on question #60760 – Chemistry – Physical Chemistry

Question:

Can solids exist in equilibrium with vapour? I'm talking about non-sublimable solids, like for example ice

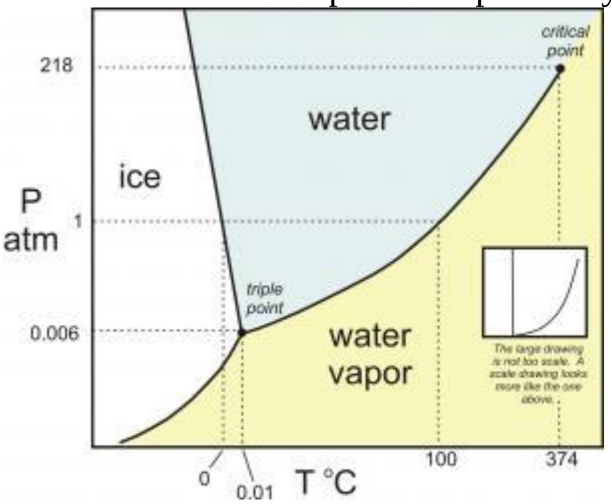
I was reading a definition which said Freezing point of a liquid is that temperature at which vapour pressure of the liquid phase equals to the vapour pressure of the solid phase. So my question is does solid exist in equilibrium with vapour? I don't get the chemistry behind it. I mean to say how can solidified molecules travel into air and form vapour?

Answer:

Yes, solid can exist in equilibrium with vapour. It can be proved by the analysis if phase diagram.

Common information.

Let's consider the simple 1 component system for H_2O:



Phase diagram for the one component system H_2O. This diagram is not to scale; a scale version looks like the thumbnail in the white box.

- The system is entirely composed of H_2O, so there is only one component present.
- The phases present represent three states of matter: liquid (water), solid (ice), and vapor (steam). All have distinct physical properties (e.g. density, structure–or lack of, etc.) and chemical properties (e.g. $\Delta G_{formation,}$ molar volume etc.) so they must be considered distinct phases.
- Note that there is only one point on this diagram where all three phases coexist in equilibrium–this "triple point" is also referred to as an *invariant point*; because P and T are uniquely specified, there are zero degrees of freedom.
- **Each of the curves represents a chemical reaction that describes a phase transformation: solid to liquid (melt/crystallization), liquid to vapor (boiling/condensation), solid to vapor (sublimation/deposition).** There are three *univariant curves* around the invariant point; it is always the case that for a C-component system, there will always be C+2 univariant curves radiating around an invariant point. This relationship is further explained in the unit on the Method of Schreinemakers. There is only one degree of

freedom along each of the univariant curves: you can independently change either T or P, but to maintain two coexisting phases along the curve the second variable must change by a corresponding fixed amount.

- There are three distinct areas where only ice, liquid, or vapor exit. These are *divariant* fields. T and P are both free to change within these fields and you will still have only one phase (a bit hotter or colder, or compressed or expanded, but nonetheless the same phase).
- The end of the "boiling curve", separating the liquid to vapor transition, is called the "critical point". This is a particularly interesting part of the phase diagram because beyond this region the physico-chemical properties of water and steam converge to the point where they are identical. Thus, beyond the critical point, we refer to this single phase as a "supercritical fluid".

So, almost all 1-components system will have phase diagrams like this. And the curves of sublimation will be present for almost all sustances (the bottom part of diagram). If the point on diagram be on curve of sublimation (you need to create defenite temperature and pressure (for water it will be T less 0.01°C, and pressure less than 0.06 atm)), solid and vapour will be in equilibrium.

Ice also can be sublimated, but defenite condition shoud be created for this!

Vapour, liquid and solid differ only distance between molecules. When solid transforms into vapour, distance between molecules is changed.