The kelvin equation

The Kelvin equation relates the vapour pressure of a liquid to the effect of surface curvature i. e. a meniscus with radius. The equation illustrates that due to the surface tension and the surface being larger than the volume, there is much higher evaporation rate for smaller droplet liquids when compared to that of larger droplets.

$\ln(P/P_0) = 2? V_m /rRT$

The Kelvin equation also shows that smaller particles exhibits higher solubility than larger particles. This occurs because of much greater pressure inside the droplet than outside and therefore gas diffusion can occur across the plateau borders of the droplet, weakening the walls (from high to low pressure). The vapour pressure of that over the droplet of water of radius r and inside a bubble in water at a specific temperature could be calculated using the Kelvin equation below.

KELVIN EQUATION PARAMETERS
P: Actual vapour pressure

P0: Saturated vapour pressure

Surface tension of liquid

MW: Molecular weight

r: Radius

Density

R: Universal gas constant (8. 314 J K-1 mol-1)

T: Temperature in Kelvin

The Kelvin equation has a variety of significant effects as it provides clarifications for such phenomena including supersaturation of vapours, superheating, Ostwald ripening and capillary condensation. This effect is known as Kelvin effect and also Gibbs-Kelvin effect or Gibbs-Thomson effect. (Barnes 2005)

Supersaturation

The effect on the Kelvin equation could be explained in terms of supersaturation of vapour. The term of supersaturation refers to the state in which a solution has overly dissolved material than that of a saturated solution. Supersaturation could also be referred to the compound's vapour having greater partial pressure than that of the vapour pressure of the compound.

In the solid form, the small particles can lead to crystallites or large single crystals formation. In a polydisperse suspension the material will dissolve until it has reached its saturated level at that temperature. When the sample is stored, the temperature will fluctuate slightly regardless of storage location. For example, if the sample is stored in the fridge, the temperature could vary and so the temperature of suspension could increase leading to a rise in saturation level allowing smaller particles to further dissolve until a new saturation level is reached. When the temperature drops, the suspension is affected in terms of consisting more than usual of the dissolved species. The new concentration is described as supersaturation. The remaining dissolved species would precipitate back on all the particles,

the smaller particles preferentially dissolve and so larger particles having a coat will enlarge. Hence, supersaturated solutions are a result because of alteration of the saturated solution, i. e. temperature, volume or pressure.

Some examples of supersaturation are beer and carbonated water. Water is able to dissolve a lot of carbon dioxide than at atmospheric pressure, which happens at the elevated pressure in bottle. At the state of atmospheric pressure, the escape of the carbon dioxide gas from the supersaturated liquid is quite slow. This process is advanced by the existence of small bubbles which is caused by shaking the product.

Rock candy
Rock candy is a type of confectionery mineral composed of relatively large sugar crystals. The candy is formed by allowing a supersaturated solution of sugar and water to crystallize onto a surface suitable for crystal nucleation, such as a string or stick…

In the phenomenon of superheating, the homogeneous substance without boiling is heated at a temperature in which is greater than the liquids normal boiling point. In order for a vapour bubble to expand and consequently burst at the surface (to boil), the temperature heating must be highly sufficient (raised above the boiling point) that the vapour pressure will go beyond the atmospheric pressure. (Patrick 2006) An insufficient temperature that is below will cause the vapour bubble to decrease and so disappear.

However, in terms of superheating, the liquid is seen that it does not boil despite having the vapour pressure exceeding the atmospheric pressure. As a result, the surface tension restrains the growth of the bubbles. Boiling

chips which are also known as boiling stones or anti-bumping granules are purposely added to the liquid to make boiling easier without the liquid becoming superheated. They are small and insoluble porous stones composing of calcium carbonate or silicon carbide. Inside the stones, they have pores that allow cavities to trap air and supply spaces in which the solvent bubbles can develop (nucleation sites i. e. formation of the vapour bubbles in on cavities).

When there is an addition of boiling chips to a solvent and is heated, it would release very small bubbles. These tiny bubbles prevent bumping, loss of solution and hence allows liquid to boil easier without being superheated. Without the addition of boiling chips in a solvent, the heated liquid could be defined as superheated, an unstable state and therefore would be able to release a quantity of bubble of gas all of a sudden or perhaps violently. As a consequence of the sudden expel of vapour from the container of the liquid, it could lead to from ruining of the experiment to causing harsh burns.

Ostwald ripening
In regards to droplets that are spherical and being in contact with their vapour, the two radii situated in the liquid phase are equal and so maintain positive signs. Therefore in reference to the Kelvin equation, the droplet's vapour pressure will be higher than the same liquid with a flat surface. An example is that for a radius of water droplet of 10nm, the increase in vapour pressure is approximately 10%. The smaller the droplets radius, the greater the vapour pressure. (Barnes 2005)

For instance, in the case a polydispersion system (droplets with different sizes), the smaller particles has the tendency to dissolve (i. e. have greater solubility) or evaporate attaching themselves onto the surface of the larger ones, leading the larger particles to continue to grow with time but the smaller particles disappearing. This spontaneous process known as Ostwald ripening was first recognised in 1896 by Wilhelm Ostwald. (Ostwald 1896)

A real life effect of the Kelvin equation occurs in clouds in which the larger droplets grow expecting to be heavy enough to fall as rain. Similarly, this process also exists for crystals contained in solutions. The larger crystals will tend to grow rather than the smaller ones resulting in a process of Ostwald ripening. This process is an important ageing effect occurring in any polydisperse systems. It could be observed in foams, emulsions as well as aqueous sols. (Adamson 1990)

In terms of foam instability, the reason of instability could be due to Ostwald ripening. The Ostwald ripening's driving force arises because of the variation of Laplace pressure between bubbles of unequal size that is the smaller and larger foam bubbles. (Barnes 2005)

The smaller bubbles having a greater gas pressure than the larger bubbles causes an effect on the foam stability. For the period of foam storage, the bubbles rise in the gravity field to the top of the liquid due to the large density existing between the liquid and the gas phases. From here, they shape a loosely closed-packed or honeycomb like structure from which the liquid drains forming foam that turns out to be dryer. The thin films created can collapse due to gravity and causing coalescence of bubbles. When

increased of gas solubility with pressure happens, gas between bubbles are able to diffuse from the smaller to the larger bubbles. A large bubble in the foam that is surrounded by smaller bubbles could ultimately cause a big hole in the structure of the foam. (Hubbard 2002)

Ostwald ripening is the cause of foam instability when a larger pressure difference of foam bubbles that are spherical cam be seen. In the case of polyhedral foam (with planar liquid lamella), the foam bubbles pressure difference is not great and so foam instability is not because of the Ostwald process. (Tadros 2005)

Since the surface of the bubble behaves like viscoelastic behaviour, the process of Ostwald ripening in foam bubbles could be reduced by addition of a gas that is only soluble in the liquid. As a result of this process, it also has an effect of decreasing of specific surface area in time due to the highly soluble particles. (Lyklema 2005) The Ostwald ripening is important as it is used to increase the efficiency in both industrial and analytical filtration. (Barnes 2005)

Capillary Condensation
The Kelvin effect can also be observed in terms of capillary condensation due to the existence of a curvature, a meniscus. Capillary condensation arises because of the vapour's adsorption in a capillary which creates a liquid surface with tiny radius of curvature. (Fisher 2002)

The liquids vapour pressure being lower than that of the same liquid with a flat surface is a consequence of the radii being positioned in the vapour phase. If the actual vapour pressure is greater than the vapour pressure

calculated from using the Kelvin equation for the curved surface than condensation would likely to occur. The actual vapour pressure for a flat surface may possibly be lower than its saturation vapour pressure. (Patrick 2006)

As the capillary filled by capillary condensation occurs, immediately a meniscus is generated (which depends on the liquids surface tension) at the liquid-vapour interface enabling the equilibrium to be under the Psat (saturation vapour pressure). At low vapour pressure, the liquid condenses in smaller radius of the capillary. As the vapour pressure increases, further condensation of the liquid at the larger radius capillary is filled causing the radius of the meniscus to increase (capillary becoming full). The Kelvin equation implies that the Pv/Psat rises inside a capillary and the meniscus radius will further expand causing a creation of more flat surface. Hence, the vapour condensation is able to occur smoothly over the range of vapour pressures. For any liquid-vapour interface involving a meniscus, the Kelvin equation therefore relates the change between the equilibrium vapour pressure and the saturation vapour pressure.

Capillary condensation as an important factor, is significant by means in both naturally and synthetic occurring porous structures. These structures allow scientists to recognize the concept of capillary condensation to determine pore size distribution as well as surface area through adsorption isotherms. (Barnes, 2005)

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