

Vapor/Liquid/Solid Equilibria:

The formation of liquid droplets from a supersaturated vapor phase and the further reaction to solid nanoparticles is a common route to large scale production of fine powders. The relationship between droplet size, r , surface tension, γ , molar volume of the liquid, v_B and saturation ratio, $S = p/p_s$, is given by the Kelvin equation,

$$\ln \frac{p}{p_s} = \frac{2 \gamma v_B}{rRT}$$

This is almost identical to the Gibbs-Thompson equation and is derived in a similar way. The Gibbs free energy for a vapor with small particles of a condensed phase is given by,

$$G = n_A \mu_A(p, T) + n_B \mu_B(p, T) + 4 \pi r^2 \gamma$$

where A and B refer to the vapor and particles. p refers to the external pressure of the vapor. At equilibrium between the particle and the vapor phase the derivative of G with respect to n_B is 0, and since $n_B = 4 \pi r^3 / (3 v_B)$,

$$0 = \mu_B - \mu_A + 4 \pi r^2 \gamma \frac{d(r^2)}{dn_B} = \mu_B - \mu_A + \frac{2 \gamma v_B}{r}$$

We have,

$$d\mu_A = \bar{v}_A dp \quad \text{and} \quad d\mu_B = \bar{v}_B dp$$

so, taking the derivative of the minimized free energy expression,

$$(\bar{v}_A - \bar{v}_B) dp = 2 \gamma v_B d \frac{1}{r}$$

Using the ideal gas law, $v_A = RT/p$, and realizing that $v_A \gg v_B$,

$$RT \frac{dp}{p} = 2 \gamma v_B d \frac{1}{r}$$

Integrating from $r = r_s$, $p = p_s$, to r and p gives the Kelvin equation above.

Laplace Equation:

The pressure inside a small liquid droplet is much higher than in the surrounding media due to surface tension. For a liquid droplet at equilibrium with its surroundings the work to add a small amount of material, dv , to a droplet is equal to that required to extend the surface,

$$(p_L - p_v)(4 r^2 dr) = (8 r dr)$$

so,

$$p = (p_L - p_v) = \frac{2}{r}$$

Droplets Containing Solute:

Typically in nanoparticle synthesis from a vapor state liquid droplets are not pure liquid but contain a fixed amount of a solute which may be the precursor to a nanopowder. As the droplet equilibrates with its environment the total mass of solute remains fixed so that the concentration may increase with diminishing particle size. The vapor pressure of the solvent, p , for such a droplet follows the Kelvin equation, $\ln \frac{p}{p_s} = \frac{2 \bar{v}_B}{rRT}$. The equilibrium vapor pressure, p_s , however, is modified by the chemical activity, a , for the solute,

$$p_s = x p_{s,0}$$

where x is the mole fraction solute. The two effects compete and can stabilize small droplets as shown in the figure of Friedlander below.

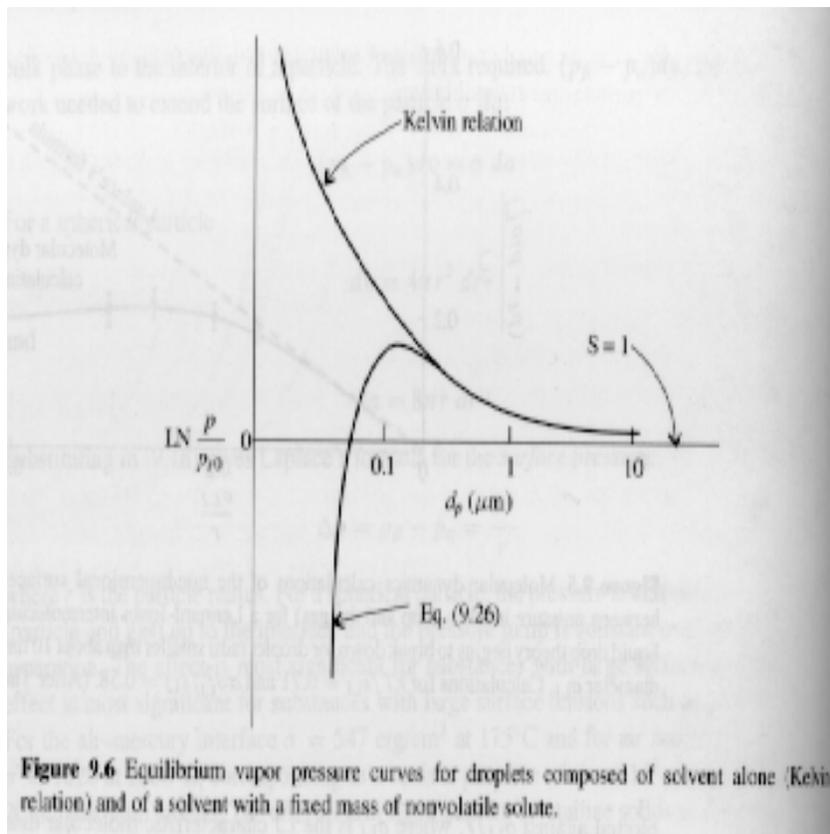


Figure 9.6 Equilibrium vapor pressure curves for droplets composed of solvent alone (Kelvin relation) and of a solvent with a fixed mass of nonvolatile solute.

From Friedlander, SK "Smoke Dust and Haze" 2000

If the volume of a droplet is decomposed into the solvent, v_1 and solute, v_2 , contributions we can write, $V_{\text{droplet}} = d_p^3/6 = n_1 v_1 + n_2 v_2$. This can be rearranged to,

$$\frac{1}{x_1} = 1 + \frac{n_2}{n_1} = 1 + \frac{n_2 \bar{v}_1}{\frac{d_p^3}{6} - n_2 \bar{v}_2}$$

substituting in the Kelvin equation yields,

$$\ln \frac{p}{p_{s0}} = \frac{4 \bar{v}_1}{d_p RT} + \ln \left(1 - \ln \left(1 + \frac{n_2 \bar{v}_1}{\frac{d_p^3}{6} - n_2 \bar{v}_2} \right) \right)$$

For an ideal solution and a dilute, non-surface active ($\gamma = 1$) solute a simplified expression is obtained,

$$\ln \frac{p}{p_{s0}} = \frac{4 \bar{v}_1}{d_p RT} - \frac{6n_2 \bar{v}_1}{d_p^3}$$

For small droplets the second term due to solute lowering of the vapor pressure dominates. This effect can lead to large super-saturations in small liquid droplets as shown by Junge, CE, "Air Chemistry and Radioactivity" 1963.

Vapor Equilibria for Charged Particles:

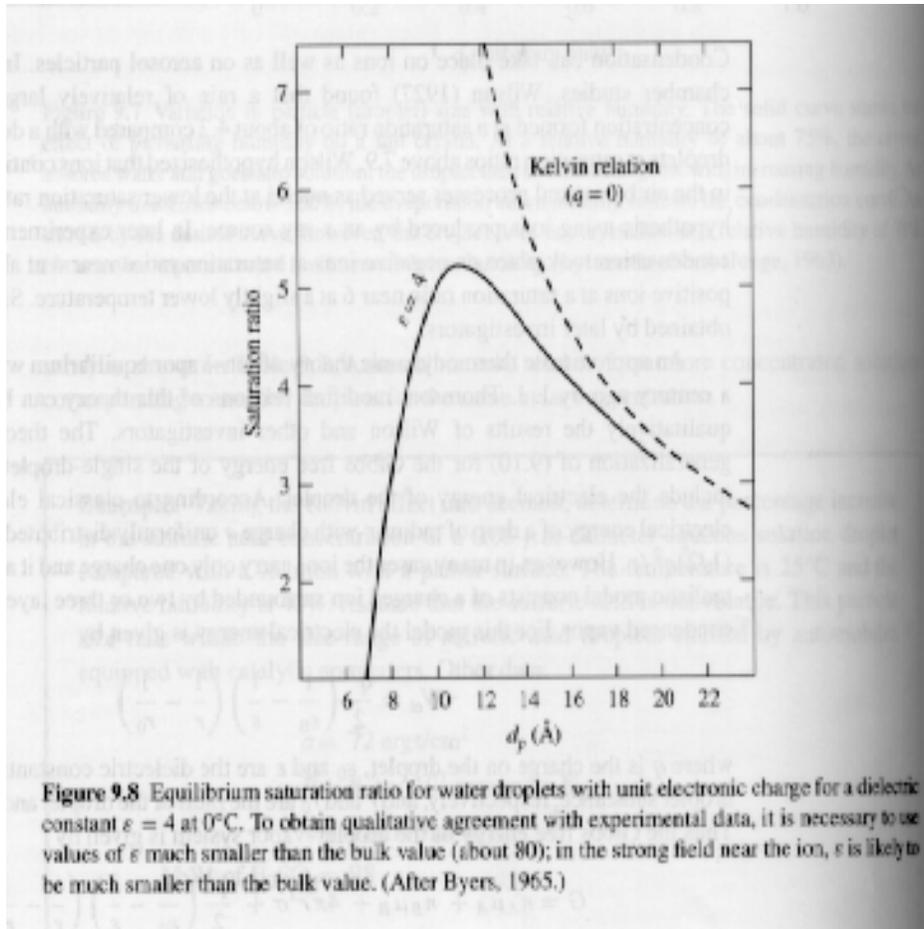
The Gibbs free energy for a droplet-vapor system with charging of the droplet by ions is given by,

$$G = n_A \mu_A(p, T) + n_B \mu_B(p, T) + 4 \pi r^2 \gamma + \frac{q^2}{2} \left(\frac{1}{r_0} - \frac{1}{r} \right) \left(\frac{1}{r} - \frac{1}{r_0} \right)$$

where r_0 is the ion radius (Angstroms) and γ_0 is usually 1 (Friedlander 2000). Following the Kelvin calculation the derivative of this free energy is set to 0 for variation of $dn_B = -dn_A$,

$$\ln \frac{p}{p_s} = \frac{2 \bar{v}_B}{r RT} - \frac{q^2 \bar{v}_B}{8 R T r^4} \left(1 - \frac{1}{r/r_0} \right)$$

Which is a similar result to the solute concentration effect except that the droplet size is two orders smaller! This ion effect was used in the cloud chamber experiments of Wilson (1927) to track subatomic particles for which he won the Nobel Prize. The figure below shows the dramatic effect of charged ions on droplet stabilization.



From Friedlander SK "Smoke Dust and Haze" 2000

Extension to Crystalline/Solid Nanoparticles:

For a solid nanoparticle of size r , the Kelvin equation can be used to describe solid/vapor equilibria. The predicted pressure within a 5nm particle of NaCl, for example, in equilibria with water vapor is on the order of 2000 bars! This is due to the relatively large surface tension of solid particles. This is one way to view the Hoffmann-Lauritzen form of the Gibbs-Thompson equation, modified to include vapor-liquid equilibria,

$$T - T_r = \frac{2T}{H_f} \left(\frac{\sigma_{SL}}{r} + 1 - \frac{\sigma_L}{L} \right)$$

(Peppiatt, Samples, Proc. Royal Soc. **345** 387.) The large pressure predicted by the Kelvin equation can also effect the equilibria of heterogeneous chemical reactions, i.e. gas phase catalysis using nanoparticle catalysts. For a gas/solid phase reaction, $_A\text{A}(\text{solid}) + _B\text{B}(\text{gas}) \rightleftharpoons _C\text{C}(\text{gas})$, the condition for chemical equilibria is given by,

$$\sum_{i=1}^N \mu_i = 0$$

If $i = 1$ is the solid phase and $i = 2$ to N are ideal gas phases, then for 2 to N ,

$$\mu_i = \mu_{i0}(T) + RT \ln p_i$$

The gas phase partial equilibrium constant, K_p , is defined by,

$$K_p = \prod_{i=2}^N p_i^{\nu_i}$$

So the condition for equilibria is,

$$-RT \ln K_p = \sum_{i=2}^N \nu_i \mu_i^0 + \nu_1 \mu_1$$

The pressure and temperature in the solid phase governs the chemical potential of component 1. Using the Laplace equation, $p = p_0 + \frac{2\sigma}{r}$,

$$\mu_1 = \mu_1^0 + \nu_1 p_s = \mu_1^0 + \frac{2\sigma \nu_1}{r}$$

and,

$$-RT \ln K_p = \sum_{i=2}^N \nu_i \mu_i^0 + \nu_1 \mu_1 = \sum_{i=2}^N \nu_i \mu_i^0 + \frac{2\sigma \nu_1}{r} = G_T^0 + \frac{2\sigma \nu_1}{r}$$

Using the partial equilibrium constant for a planar surface, $K_{p,0}$,

$$-RT \ln \frac{K_p}{K_{p,0}} = \frac{2\sigma \nu_1}{r}$$

This equation indicates that nano-particle catalysts enhance the reactivity for heterogeneous gas/solid phase reactions due to the Laplace enhancement of pressure in small particles that enhances thermodynamic activity.

Growth of Liquid Clusters from the Vapor Phase:

For a gas that is condensable into a liquid cluster containing g molecules we can write, $A_{g-1} + A_1 \rightleftharpoons A_g$. This is similar to the liquid phase reaction considered earlier except that a gas phase monomer immediately attaches to the liquid phase cluster on approach, while the liquid phase must go through an evaporative process to be released from the liquid cluster. If s_g is the surface area for a g -cluster, J_g is the evaporative flux and J_{g-1} is the monomer flux to the cluster,

$$s_{g-1} J_{g-1} = s_g J_g$$

at equilibrium and below the saturation vapor pressure. The kinetic theory of gasses gives the flux to the cluster,

$$= \frac{p_1}{(2 mkT)^{1/2}}$$

where p_1 is the monomer partial pressure and m is the monomer mass. The evaporative flux is given by the Kelvin equation,

$$j_s = \frac{p_s}{(2 mkT)^{1/2}} \exp \frac{4 v_m}{d_p kT}$$

where p_s is for a flat surface. By using these expressions in the rate balance above,

$$\frac{n_{g-1}}{n_g} = \frac{1}{S} \exp \frac{2 v_m \frac{4}{3v_m} \frac{1}{g^3 kT}}$$

where $S = p_1/p_s$. From this ratio the particle size distribution can be calculated,

$$n_g = n_s S^g \exp \frac{-3 v_m \frac{4}{3v_m} g^{\frac{1}{3}} \frac{2}{g^3}}{kT}$$

where $n_s = p_s/kT$, and $S = p_1/p_s$. For $S < 1$ the function decays with g . For $S > 1$ the function has a minimum at d_p^* given by,

$$d_p^* = \frac{4 v_m}{kT \ln S}$$

The number of critical nuclei is given by,

$$n_g^* = n_1 \exp \frac{-16 v_m^2}{3(kT)^3 (\ln S)^2}$$