2.5 The Kelvin equation

In this chapter we get to know the second essential equation of surface science — the Kelvin[5] equation. Like the Young–Laplace equation it is based on thermodynamic principles and does not refer to a special material or special conditions. The subject of the Kelvin equation is the vapor pressure of a liquid. Tables of vapor pressures for various liquids and different temperatures can be found in common textbooks or handbooks of physical chemistry. These vapor pressures are reported for vapors which are in thermodynamic equilibrium with liquids having planar surfaces. When the liquid surface is curved, the vapor pressure changes. The vapor pressure of a drop is higher than that of a flat, planar surface. In a bubble the vapor pressure is reduced. The Kelvin equation tells us how the vapor pressure depends on the curvature of the liquid.

The cause for this change in vapor pressure is the Laplace pressure . The raised Laplace pressure in a drop causes the molecules to evaporate more easily. In the liquid, which surrounds a bubble, the pressure with respect to the inner part of the bubble is reduced. This makes it more difficult for molecules to evaporate. Quantitatively the change of vapor pressure for curved liquid surfaces is described by the Kelvin equation:

$$RT \cdot \ln \frac{P_0^K}{P_0} = \gamma V_m \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{2.17}$$

P_0^K is the vapor pressure of the curved, P_0 that of the flat surface. The index "0" indicates that everything is only valid in thermodynamic equilibrium. Please keep in mind: in equilibrium the curvature of a liquid surface is constant everywhere. V_m is the molar volume of the liquid. For a sphere-like volume of radius r, the Kelvin equation can be simplified:

$$RT \cdot \ln \frac{P_0^K}{P_0} = \frac{2\gamma V_m}{r} \qquad \text{or} \qquad P_0^K = P_0 \cdot e^{\frac{2\gamma V_m}{RTr}} \tag{2.18}$$

The constant $2\gamma V_m / RT$ is 1.03 nm for Ethanol ($\gamma = 0.022$ N/m, $V_m = 58$ cm^3/mol) and 1.05 nm for Water ($\gamma = 0.072$ N/m, $V_m = 18$ cm^3/mol) at 25°C.

To derive the Kelvin equation we consider the Gibbs free energy of the liquid. The molar Gibbs free energy changes when the surface is being curved, because the pressure increases

[5] William Thomson, later Lord Kelvin, 1824–1907. Physics professor at the University of Glasgow.

due to the Laplace pressure. In general, any change in the Gibbs free energy is given by the fundamental equation $dG = VdP - SdT$. The increase of the Gibbs free energy per mole of liquid, upon curving, at constant temperature is

$$\Delta G_m = \int_0^{\Delta P} V_m dP = \gamma V_m \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{2.19}$$

We have assumed that the molar volume remains constant, which is certainly a reasonable assumption because most liquids are practically incompressible for the pressures considered. For a spherical drop in its vapor, we simply have $\Delta G_m = 2\gamma V_m / r$. The molar Gibbs free energy of the vapor depends on the vapor pressure P_0 according to

$$G_m = G_m^0 + RT \cdot \ln P_0 \tag{2.20}$$

For a liquid with a curved surface we have

$$G_m^K = G_m^0 + RT \cdot \ln P_0^K \tag{2.21}$$

The change of the molar Gibbs free energy inside the vapor due to curving the interface is therefore

$$\Delta G_m = G_m^K - G_m = RT \cdot \ln \frac{P_0^K}{P_0} \tag{2.22}$$

Since the liquid and vapor are supposed to be in equilibrium, the two expressions must be equal. This immediately leads to the Kelvin equation.

When applying the Kelvin equation, it is instructive to distinguish two cases: A drop in its vapor (or more generally: a positively curved liquid surface) and a bubble in liquid (a negatively curved liquid surface).

Drop in its vapor: The vapor pressure of a drop is higher than that of a liquid with a planar surface. One consequence is that an aerosol of drops (fog) should be unstable. To see this, let us assume that we have a box filled with many drops in a gaseous environment. Some drops are larger than others. The small drops have a higher vapor pressure than the large drops. Hence, more liquid evaporates from their surface. This tends to condense into large drops. Within a population of drops of different sizes, the bigger drops will grow at the expense of the smaller ones — a process called Ostwald ripening[6]. These drops will sink down and, at the end, bulk liquid fills the bottom of the box.

For a given vapor pressure, there is a critical drop size. Every drop bigger than this size will grow. Drops at a smaller size will evaporate. If a vapor is cooled to reach over-saturation, it cannot condense (because every drop would instantly evaporate again), unless nucleation sites are present. In that way it is possible to explain the existence of over-saturated vapors and also the undeniable existence of fog.

Bubble in a liquid: From Eq. (2.19) we see that a negative sign has to be used for a bubble because of the negative curvature of the liquid surface. As a result we get

$$RT \cdot \ln \frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r} \tag{2.23}$$

[6] In general, Ostwald ripening is the growth of long objects at the expense of smaller ones. Wilhelm Ostwald, 1853–1932. German physicochemist, professor in Leipzig, Nobel price for chemistry 1909.

Here, r is the radius of the bubble. The vapor pressure inside a bubble is therefore reduced. This explains why it is possible to overheat liquids: When the temperature is increased above the boiling point (at a given external pressure) occasionally, tiny bubbles are formed. Inside the bubble the vapor pressure is reduced, the vapor condenses, and the bubble collapses. Only if a bubble larger than a certain critical size is formed, is it more likely to increases in size rather than to collapse. As an example, vapor pressures for water drops and bubbles in water are given in Table 2.2.

r (nm)	P_0^K/P_0 drop	P_0^K/P_0 bubble
1000	1.001	0.999
100	1.011	0.989
10	1.114	0.898
1	2.950	0.339

Table 2.2: Relative equilibrium vapor pressure of a curved water surface at 25°C for spherical drops and bubbles of radius r.

At this point it is necessary to clarify several questions which sometimes cause confusion. When do we use the term "vapor" instead of "gas"? Vapor is used when the liquid is present in the system and liquid evaporation and vapor condensation take place. This distinction is not always clear cut because, when dealing with adsorption (Chapter 9) we certainly take the two corresponding processes — adsorption and desorption — into account but still talk about gas. How does the presence of an additional background gas change the properties of a vapor? For example, does pure water vapor behave differently from water vapor at the same partial pressure in air (in the presence of nitrogen and oxygen)? Answer: To a first approximation there is no difference as long as phenomena in thermodynamic equilibrium are concerned. "First approximation" means, as long as interactions between the vapor molecules and the molecules of the background gas are negligible. However, time-dependent processes and kinetic phenomena such as diffusion can be completely different and certainly depend on the background gas. This is, for instance, the reason why drying in a vacuum is much faster than drying in air.

2.6 Capillary condensation

An important application of the Kelvin equation is the description of capillary condensation. This is the condensation of vapor into capillaries or fine pores even for vapor pressures below P_0; P_0 is the equilibrium vapor pressure of the liquid with a planar surface. Lord Kelvin was the one who realized that the vapor pressure of a liquid depends on the curvature of its surface. In his words this explains why "moisture is retained by vegetable substances, such as cotton cloth or oatmeal, or wheat-flour biscuits, at temperatures far above the dew point of the surrounding atmosphere" [17].

Capillary condensation can be illustrated by the model of a conical pore with a totally wetting surface (Fig. 2.12). Liquid will immediately condense in the tip of the pore. Condensation continues until the bending radius of the liquid has reached the value given by the Kelvin equation. The situation is analogous to that of a bubble and we can write

$$RT \cdot \ln \frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r_C} \tag{2.24}$$