Chapter 8
Trouton’s Rule

The rule of Trouton\textsuperscript{1} states that the entropy of vaporization at the boiling point is for all substances approximately

\[ \Delta \tilde{S}_v = \Delta \tilde{H}_v / T_b \approx 90 \text{ J mol}^{-1} \text{K}^{-1}. \]

Trouton’s rule was published in 1883 and after the 100 years anniversary, several papers with historical remarks appeared [1–3].

Guggenheim has collected data and expressed phase equilibria in terms of corresponding states [4]. The modeling of the coexistence equations with regard to the liquid – gas equilibrium is still an object of research [5].

8.1 Dimensionless Variables

We start with the well-known relations

\[ \frac{dp}{dT} = \frac{\Delta \tilde{S}_v}{\Delta \tilde{V}_v}. \] (8.1)

Here \( \Delta \tilde{S}_v \) is the entropy of vaporization and \( \Delta \tilde{V}_v \) is the volume change on vaporization. Using now

\[ dp = p \, d \ln p, \quad dT = -T^2 \, d \left( \frac{1}{T} \right), \quad \tilde{T} = \frac{T}{T_c}, \quad \tilde{p} = \frac{p}{p_c}, \]

we obtain from Eq. (8.1)

\[ \frac{d \ln \tilde{p}}{d1/\tilde{T}} = -\frac{T \Delta \tilde{S}_v}{p \Delta \tilde{V}_v} \tilde{T}. \] (8.2)

\textsuperscript{1} Frederick Thomas Trouton, born Nov. 24, 1863, in Dublin, Ireland, died Sep. 21, 1922, in Downe, Kent.
$T_c$ is the critical temperature and $\tilde{T}$ is the reduced temperature. The same notation is used for the pressure.

In Eq. (8.2), only reduced, dimensionless variables appears, and this equation should no be longer dependent on the individual properties of the materials. Note that $T \Delta S/p \Delta V$ is some ratio of thermal energy to volume energy.

In fact, a close similarity for the various substances is monitored; however, it can be seen that the monoatomic gases are separated from the polyatomic gases. The difference is not very much pronounced, however, and we neglect this difference here. Further, we deal with the plot as a straight line as a first approximation. Under these conditions, immediately

$$\frac{p \Delta \tilde{V}_v}{T \Delta \tilde{S}_v} = \tilde{T} \Theta(\tilde{T})$$

(8.3)

follows. $\Theta(\tilde{T})$ is a function of $\tilde{T}$. At the left-hand side of Eq. (8.3), there appears a ratio of energies. This is the energy of expansion when the liquid expands on vaporization, and some sort of thermal energy that must be delivered on vaporization. In fact, it is the enthalpy of vaporization.

In the present form, Eq. (8.3) resembles the law of Wiedemann,\textsuperscript{2} Franz,\textsuperscript{3} and Lorenz\textsuperscript{4}. We can also interpret the left-hand side as a degree of efficiency with regard to mechanical and to thermal work. In the region of low pressures, the vapor approaches an ideal gas. Here Eq. (8.2) becomes

$$\frac{d \ln \tilde{p}}{d \frac{1}{\tilde{T}}} = -\frac{\Delta \tilde{H}_v}{R T_c}.$$  

(8.4)

A plot of the logarithm of the reduced pressure against the reciprocal reduced temperature is shown in Fig. 8.1. The equation of Clausius – Clapeyron reads as

$$\frac{d \ln p}{d 1/T} = -\frac{\Delta \tilde{H}_v}{R}.$$  

(8.5)

If we rewrite the equation of Clausius – Clapeyron (Eq. 8.5) in reduced quantities, we obtain simply Eq. (8.4).

For substances that obey the theorem of corresponding states, the term $\Delta \tilde{H}_v / RT_c$ should be a universal constant, or more generally a function of the reduced temperature only. It has been pointed out by Guggenheim\textsuperscript{4} that $\Delta \tilde{H}_v / T$ at corresponding temperatures, i.e., temperatures being the same fraction of the critical temperature, has always the same numerical value.

\textsuperscript{2} Gustav Heinrich Wiedemann, born Oct. 2, 1826, in Berlin, Germany, died Mar. 23, 1899, in Leipzig, Germany.

\textsuperscript{3} Rudolph Franz, born Dec. 16, 1826, in Berlin, Germany, died Dec. 31, 1902, in Berlin, Germany.

\textsuperscript{4} Ludvig Lorenz, born Jan. 18, 1829, in Helsingør, Dutch, died Jun. 9, 1891.