

The condition at the azeotrope is discussed for multi-component mixture. Along the VLE surface, we can consider either liquid branch, with composition  $\{x_i\} = \{x_1, x_2, \dots, x_r\}$ , and vapor branch, with composition  $\{y_i\} = \{y_1, y_2, \dots, y_r\}$ , respectively, where  $r$  is the number of component. The VLE condition requires that the chemical potentials of all the components are equal in liquid or vapor phases, i.e.,

$$\mu_i^l = \mu_i^v, \quad (i = 1, 2, \dots, r).$$

Within each phase, the chemical potentials are constrained by the Gibbs-Duhem relation:

$$\begin{aligned} \sum_{i=1}^r x_i d\mu_i^l &= -s^l dT + v^l dP, \\ \sum_{i=1}^r y_i d\mu_i^v &= -s^v dT + v^v dP. \end{aligned}$$

Above,  $s^l$  and  $s^v$  are molar entropy and  $v^l$  and  $v^v$  are molar volume, in liquid and vapor phases respectively. Because  $\mu_i^l = \mu_i^v$  along the VLE, we do not need to differentiate them, and can simply write  $\mu_i \equiv \mu_i^l = \mu_i^v$  and  $d\mu_i = d\mu_i^l = d\mu_i^v$ . Then taking the difference of the two Gibbs-Duhem conditions, we get

$$\sum_{i=1}^r (y_i - x_i) d\mu_i = -\Delta s dT + \Delta v dP, \quad (*)$$

where  $\Delta s \equiv s^v - s^l > 0$ , and  $\Delta v \equiv v^v - v^l > 0$ , are molar entropy and volume change due to vaporization of liquid mixture. The variations above,  $d\mu_i$ ,  $dT$ , and  $dP$  are understood to be occurring on the VLE surface. In essence, it generalizes the Clapeyron equation to mixtures.

At the azeotrope point, we have  $y_i = x_i$  for  $i = 1, 2, \dots, r$ . Equation (\*) reduces to

$$0 = -\Delta s dT + \Delta v dP.$$

Therefore  $dP = 0$  when temperature is fixed, and  $dT = 0$  when pressure is fixed. In either case, pressure or temperature is extremized.

To show that “pressure is maximized when temperature is minimized”, we need to consider the higher order variation. We can move from the azeotrope, which is a single point on the VLE surface, along an arbitrary path. For concreteness, we can parameterize this path by, e.g.,  $\lambda$ . Then, the first order variation  $dP$  at fixed temperature is given, following eq. (\*), by

$$\Delta v \frac{dP}{d\lambda} = \sum_{i=1}^r (y_i - x_i) \frac{d\mu_i}{d\lambda}.$$

Differentiating both sides against  $\lambda$  (since we want curvature) leads to

$$\Delta v \frac{d^2 P}{d\lambda^2} + \frac{d\Delta v}{d\lambda} \frac{dP}{d\lambda} = \sum_{i=1}^r \left[ \frac{d(y_i - x_i)}{d\lambda} \frac{d\mu_i}{d\lambda} + (y_i - x_i) \frac{d^2 \mu_i}{d\lambda^2} \right].$$

At the azeotrope, we have  $\frac{dP}{d\lambda} = 0$  and  $x_i = y_i$ . The above reduces to

$$\Delta v \frac{d^2 P}{d\lambda^2} = \sum_{i=1}^r \frac{d(y_i - x_i)}{d\lambda} \frac{d\mu_i}{d\lambda}. \quad (a)$$

In full analogy, it is straightforward to show that, at fixed  $P$ ,

$$-\Delta s \frac{d^2 T}{d\lambda^2} = \sum_{i=1}^r \frac{d(y_i - x_i)}{d\lambda} \frac{d\mu_i}{d\lambda}. \quad (b)$$

We notice that the right sides of eqs. (a) and (b) are identical,  $\Delta v > 0$ , and  $-\Delta s < 0$ . So the curvatures  $\frac{d^2 P}{d\lambda^2}$  and  $\frac{d^2 T}{d\lambda^2}$  have opposite signs. One is maximized when the other is minimized.