2.H.2. Conditions for Local Stability in a PVT System

Just as the 1st order changes in S leads to the stability conditions (2.163-5) on the 1st order partials of S, the 2nd order changes in S gives us the signs of the response functions.

Instead of using the Taylor expansion, we shall derive the 2nd order change in S from the 1st order change [see (2.161)]

$$\Delta S = \sum_\alpha \Big[\left(\frac{\partial S}{\partial U_\alpha}\right)_{\{V_\beta\},\{N_{j\beta}\}} \Delta U_\alpha + \left(\frac{\partial S}{\partial V_\alpha}\right)_{U,\{V_{\beta\neq\alpha}\},\{N_{j\beta}\}} \Delta V_\alpha + \sum_{j=1}^{l} \left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{U,\{V_\beta\},\{N_{k\neq j,\beta\neq\alpha}\}} \Delta N_{j\alpha} \Big]$$

as an additional change in the coefficients so that

$$\Delta^2 S = \frac{1}{2} \sum_\alpha \Big[\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)_{\{V_\beta\},\{N_{j\beta}\}} \Delta U_\alpha + \Delta\left(\frac{\partial S}{\partial V_\alpha}\right)_{U,\{V_{\beta\neq\alpha}\},\{N_{j\beta}\}} \Delta V_\alpha + \sum_{j=1}^{l} \Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{U,\{V_\beta\},\{N_{k\neq j,\beta\neq\alpha}\}} \Delta N_{j\alpha} \Big] \qquad (2.169)$$

Note that the Taylor expansion can be recovered if we expand the coefficient changes in terms of the state variable changes, i.e.,

$$\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)_{\{V_\beta\},\{N_{j\beta}\}} = \left(\frac{\partial^2 S}{\partial U_\alpha^2}\right)_{\{V_\beta\},\{N_{j\beta}\}} \Delta U_\alpha + \left[\frac{\partial}{\partial V_\alpha}\left(\frac{\partial S}{\partial U_\alpha}\right)_{\{V_\beta\},\{N_{j\beta}\}}\right]_{U,\{V_{\beta\neq\alpha}\},\{N_{j\beta}\}} \Delta V_\alpha + \sum_j \left[\frac{\partial}{\partial N_{j\alpha}}\left(\frac{\partial S}{\partial U_\alpha}\right)_{\{V_\beta\},\{N_{k\beta}\}}\right]_{U,\{V_\beta\},\{N_{k,\beta\neq\alpha}\}} \Delta N_{j\alpha} \qquad (2.167)$$

and similarly for $\Delta\left(\frac{\partial S}{\partial V_\alpha}\right)_{U,\{V_{\beta\neq\alpha}\},\{N_{j\beta}\}}$ and $\Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{U,\{V_\beta\},\{N_{k\neq j,\beta\neq\alpha}\}}$. The overall factor $\frac{1}{2}$ is required to make (2.169) compatible with the Taylor expansion.

Using (2.58-60), we can write (2.169) as

$$\Delta^2 S = \frac{1}{2} \sum_\alpha \Big[\Delta\left(\frac{1}{T_\alpha}\right) \Delta U_\alpha + \Delta\left(\frac{P_\alpha}{T_\alpha}\right) \Delta V_\alpha - \sum_{j=1}^{l} \Delta\left(\frac{\mu_{j\alpha}'}{T_\alpha}\right) \Delta N_{j\alpha} \Big] \qquad (2.170)$$

$$= \frac{1}{2} \sum_\alpha \Big[-\frac{1}{T_\alpha^2} \Delta T_\alpha \left(\Delta U_\alpha + P_\alpha \Delta V_\alpha - \sum_{j=1}^{l} \mu_{j\alpha}' \Delta N_{j\alpha}\right) + \frac{1}{T_\alpha}\left(\Delta P_\alpha \Delta V_\alpha - \sum_{j=1}^{l} \Delta \mu_{j\alpha}' \Delta N_{j\alpha}\right) \Big]$$

$$= -\frac{1}{2T} \sum_\alpha \left(\Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_{j=1}^{l} \Delta \mu_{j\alpha}' \Delta N_{j\alpha} \right) \qquad (2.171)$$

where we have used the 1st law

$$\sum_\alpha \left(\Delta U_\alpha - T \Delta S_\alpha + P \Delta V_\alpha - \sum_{j=1}^{l} \mu_j' \Delta N_{j\alpha} \right) = 0$$

with the equilibrium conditions

$$T_\alpha = T \qquad P_\alpha = P \qquad \mu_{j\alpha}' = \mu_j' \qquad \forall\ \alpha$$

Choosing $(T, P, \{N_j\})$ as the independent variables, we have

$$\Delta S_\alpha = \left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha + \left(\frac{\partial S}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha + \sum_{j=1}^{l} \left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} \Delta N_{j\alpha} \tag{2.172}$$

$$\Delta V_\alpha = \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha + \sum_{j=1}^{l} \left(\frac{\partial V}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} \Delta N_{j\alpha} \tag{2.173}$$

$$\Delta \mu_{j\alpha}' = \left(\frac{\partial \mu_j'}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha + \left(\frac{\partial \mu_j'}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha + \sum_{k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \tag{2.174}$$

Hence,

$$\Delta T_\alpha \Delta S_\alpha = \left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 + \left(\frac{\partial S}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta T_\alpha \Delta P_\alpha + \sum_{j=1}^{l} \left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} \Delta T_\alpha \Delta N_{j\alpha}$$

$$\Delta P_\alpha \Delta V_\alpha = \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha \Delta P_\alpha + \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} (\Delta P_\alpha)^2 + \sum_{j=1}^{l} \left(\frac{\partial V}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} \Delta P_\alpha \Delta N_{j\alpha}$$

$$\Delta \mu_{j\alpha}' \Delta N_{j\alpha} = \left(\frac{\partial \mu_j'}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha \Delta N_{j\alpha} + \left(\frac{\partial \mu_j'}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha \Delta N_{j\alpha} + \sum_{k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha}$$

(2.171) thus becomes

$$\begin{aligned}\Delta^2 S = -\frac{1}{2T}\sum_\alpha \Bigg\{ & \left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 + \left[\left(\frac{\partial S}{\partial P}\right)_{T,\{N_{\alpha j}\}} - \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}}\right] \Delta T_\alpha \Delta P_\alpha \\ & + \sum_{j=1}^{l}\left[\left(\frac{\partial S}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} + \left(\frac{\partial \mu_j'}{\partial T}\right)_{P,\{N_{\alpha j}\}}\right] \Delta T_\alpha \Delta N_{j\alpha} \\ & - \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} (\Delta P_\alpha)^2 + \sum_{j=1}^{l}\left[-\left(\frac{\partial V}{\partial N_{j\alpha}}\right)_{T,P,\{N_{k\neq j,\alpha}\}} + \left(\frac{\partial \mu_j'}{\partial P}\right)_{T,\{N_{\alpha j}\}}\right] \Delta P_\alpha \Delta N_{j\alpha} \\ & + \sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}\end{aligned}$$

Using the Maxwell relations (2.112-5), we have

$$\begin{aligned}\Delta^2 S = -\frac{1}{2T}\sum_\alpha \Bigg\{ & \left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 - 2\left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha \Delta P_\alpha \\ & - \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} (\Delta P_\alpha)^2 + \sum_{j.k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}\end{aligned} \tag{2.175}$$

$$< 0 \qquad [\ S \text{ is a maximum.}\ ] \tag{2.175a}$$

Using (2.8), we have

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} &= \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} + \left(\frac{\partial S}{\partial V}\right)_{T,\{N_{\alpha j}\}} \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \\ &= \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} + \left(\frac{\partial P}{\partial T}\right)_{V,\{N_{\alpha j}\}} \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \qquad [\ (2.100) \text{ used.}\ ]\end{aligned}$$

$$= \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} \left(\frac{\partial V}{\partial T}\right)^2_{P,\{N_{\alpha j}\}} \qquad \text{[(2.6) used.]} \tag{2.176}$$

(2.175a) becomes

$$\Delta^2 S = -\frac{1}{2T}\sum_{\alpha}\Bigg\{ \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} \left(\frac{\partial V}{\partial T}\right)^2_{P,\{N_{\alpha j}\}} (\Delta T_\alpha)^2$$

$$- 2\left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha \Delta P_\alpha - \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} (\Delta P_\alpha)^2$$

$$+ \sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}$$

$$= -\frac{1}{2T}\sum_{\alpha}\Bigg\{ \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} \Bigg[\left(\frac{\partial V}{\partial T}\right)^2_{P,\{N_{\alpha j}\}} (\Delta T_\alpha)^2$$

$$+ 2\left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha \Delta P_\alpha + \left(\frac{\partial V}{\partial P}\right)^2_{T,\{N_{\alpha j}\}} (\Delta P_\alpha)^2 \Bigg]$$

$$+ \sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}$$

$$= -\frac{1}{2T}\sum_{\alpha}\Bigg\{ \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} (\Delta T_\alpha)^2$$

$$- \left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} \Bigg[\left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha \Bigg]^2$$

$$+ \sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}$$

$$= -\frac{1}{2T}\sum_{\alpha}\Bigg\{ \left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} (\Delta T_\alpha)^2 - \left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} [\Delta V_\alpha]^2_{\{N_{\alpha j}\}} \tag{2.177}$$

$$+ \sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} \Bigg\}$$

where [see (2.173)]

$$[\Delta V_\alpha]_{\{N_{\alpha j}\}} = \left(\frac{\partial V}{\partial T}\right)_{P,\{N_{\alpha j}\}} \Delta T_\alpha + \left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} \Delta P_\alpha \tag{2.178}$$

Since $(\Delta T_\alpha, \Delta P_\alpha, \{\Delta N_{j\alpha}\})$ are arbitrary variations, (2.175a) can be satisfied if and only if

$$\left(\frac{\partial S}{\partial T}\right)_{V,\{N_{\alpha j}\}} > 0 \tag{2.179a}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,\{N_{\alpha j}\}} < 0 \tag{2.179b}$$

and

$$\sum_{j,k=1}^{l} \left(\frac{\partial \mu_j'}{\partial N_{k\alpha}}\right)_{T,P,\{N_{m\neq k,\alpha}\}} \Delta N_{k\alpha} \Delta N_{j\alpha} > 0 \tag{2.179c}$$

In terms of the response functions, (2.179a-b) become

$$C_{V,\{N_{\alpha j}\}} = T\left(\frac{\partial S}{\partial T}\right)_{P,\{N_{\alpha j}\}} > 0 \qquad (2.179d)$$

$$\kappa_{T,\{N_{\alpha j}\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_{\alpha j}\}} > 0 \qquad (2.179e)$$

Putting (2.179d-e) into (2.150) of §2.G.2, we obtain the conditions for thermal stability,

$$C_{P,\{N_{\alpha j}\}} > C_{V,\{N_{\alpha j}\}} > 0 \qquad (2.180)$$

(2.151) then gives

$$\kappa_{T,\{N_{\alpha j}\}} > \kappa_{S,\{N_{\alpha j}\}} \qquad (2.180a)$$

With the help of (2.152), we get the conditions for mechanical stability,

$$\kappa_{T,\{N_{\alpha j}\}} > \kappa_{S,\{N_{\alpha j}\}} > 0 \qquad (2.181)$$

The quadratic (2.179c) can be written in matrix form as

$$Q = \boldsymbol{N}^T \mathbb{M}\, \boldsymbol{N} > 0 \qquad (2.182)$$

where T is the transpose operator and

$$\mathbb{M} = \{M_{jk}\} = \left\{\left(\frac{\partial \mu_j'}{\partial N_k}\right)_{T,P}\right\} \qquad \boldsymbol{N}^T = (N_1, \ldots, N_l) \qquad (2.183)$$

The condition (2.181a) means that $\mathbb{M}$ is a positive definite matrix.

Owing to the Maxwell relation [see (2.115)],

$$\left(\frac{\partial \mu_j'}{\partial N_k}\right)_{T,P} = \left(\frac{\partial \mu_k'}{\partial N_j}\right)_{T,P}$$

we have

$$M_{jk} = M_{kj} \quad \rightarrow \quad \mathbb{M} \text{ is a (real) symmetric matrix.}$$

The set of eigenvectors $\{\boldsymbol{V}_j\}$ of $\mathbb{M}$ can therefore be chosen to be orthonormal and span the vector space on which $\mathbb{M}$ operates. Hence, (2.181a) can be written as

$$Q = \sum_{j,k} c_j\, c_k\, \boldsymbol{V}_j^T \mathbb{M}\, \boldsymbol{V}_k \qquad \left[\ \boldsymbol{N} = \sum_k c_k \boldsymbol{V}_k \text{ used. } \right]$$

$$= \sum_{j,k} c_j\, c_k\, \lambda_k\, \boldsymbol{V}_j^T \boldsymbol{V}_k \qquad \left[\ \mathbb{M}\, \boldsymbol{V}_k = \lambda_k \boldsymbol{V}_k \text{ used. } \right]$$

$$= \sum_j c_j^2\, \lambda_j \qquad \left[\ \boldsymbol{V}_j^T \boldsymbol{V}_k = \delta_{jk} \text{ used. } \right]$$

Hence,

$$Q > 0 \quad \Leftrightarrow \quad \lambda_j > 0 \quad \forall\ j \qquad (2.183a)$$

Thus, $\mathbb{M}$ is positive definite (i.e., $\mathbb{M} > 0$) if its eigenvalues are all positive definite.

There are many equivalent criteria for positive-definiteness. For example, the Sylvester's criteria states that a Hermitian matrix $\mathbb{M}$ is positive definite if and only if every one of its leading principal minors is positive definite. The k^{th} leading principal minor $m^{(k)}$ of $\mathbb{M}$ is the determinant of its upper-left $k \times k$ submatrix. Thus,

$$\mathbb{M} > 0 \quad \Leftrightarrow \quad m^{(k)} > 0 \quad \forall\ k \qquad (2.183b)$$

In particular,

$$\mathbb{M} > 0 \qquad \rightarrow \qquad m^{(1)} = M_{11} > 0 \qquad (2.183c)$$

Since the positivity of a matrix is not affected by rearranging the rows or columns. (2.181c) implies

$$\mathbb{M} > 0 \qquad \rightarrow \qquad M_{jj} > 0 \qquad \forall\ j \qquad (2.183d)$$

i.e., the diagonal elements of a positive Hermitian matrix must all be positive definite.

Ex.2.9.

A mixture of two types of particles A and B has a Gibbs free energy of the form

$$G = n_A\,\mu_A^0(T,P) + n_B\,\mu_B^0(T,P) + R\,T\,n_A \ln x_A + R\,T\,n_B \ln x_B + \lambda\,\frac{n_A\,n_B}{n} \qquad (1a)$$

where

$$n = n_A + n_B \qquad x_k = \frac{n_k}{n} \quad \text{for} \quad k = A, B \qquad (1b)$$

Plot the region of thermodynamic instability in the x_A-T plane.

Answer

According to (2.182), the criterion for chemical stability is

$$\mathbb{M} = \begin{pmatrix} \left(\frac{\partial \mu_A}{\partial n_A}\right)_{T,P} & \left(\frac{\partial \mu_A}{\partial n_B}\right)_{T,P} \\ \left(\frac{\partial \mu_B}{\partial n_A}\right)_{T,P} & \left(\frac{\partial \mu_B}{\partial n_B}\right)_{T,P} \end{pmatrix} > 0 \qquad (1)$$

(2.183b) then requires

$$\left(\frac{\partial \mu_A}{\partial n_A}\right)_{T,P} > 0 \qquad \left(\frac{\partial \mu_B}{\partial n_B}\right)_{T,P} > 0 \qquad (1c)$$

&

$$\det \begin{vmatrix} \left(\frac{\partial \mu_A}{\partial n_A}\right)_{T,P} & \left(\frac{\partial \mu_A}{\partial n_B}\right)_{T,P} \\ \left(\frac{\partial \mu_B}{\partial n_A}\right)_{T,P} & \left(\frac{\partial \mu_B}{\partial n_B}\right)_{T,P} \end{vmatrix} > 0$$

$$\rightarrow \left(\frac{\partial \mu_A}{\partial n_A}\right)_{T,P} \left(\frac{\partial \mu_B}{\partial n_B}\right)_{T,P} > \left(\frac{\partial \mu_A}{\partial n_B}\right)_{T,P}^2 \qquad \left[\ \left(\frac{\partial \mu_A}{\partial n_B}\right)_{T,P} = \left(\frac{\partial \mu_B}{\partial n_A}\right)_{T,P} \text{ used. } \right] \qquad (1d)$$

Using

$$\frac{\partial x_A}{\partial n_A} = \frac{\partial}{\partial n_A}\left(\frac{n_A}{n}\right) = \frac{1}{n} - \frac{n_A}{n^2} = \frac{n_B}{n^2}$$

$$\frac{\partial x_B}{\partial n_A} = \frac{\partial}{\partial n_A}\left(\frac{n_B}{n}\right) = -\frac{n_B}{n^2}$$

on (1a) gives

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} = \mu_A^0(T,P) + R\,T\left(\ln x_A + \frac{n_A}{x_A}\frac{n_B}{n^2} - \frac{n_B}{x_B}\frac{n_B}{n^2}\right) + \lambda\left(\frac{n_B}{n} - \frac{n_A\,n_B}{n^2}\right)$$

$$= \mu_A^0(T,P) + R\,T \ln x_A + \lambda\,\frac{n_B^2}{n^2} \qquad (2)$$

Taking $A \leftrightarrow B$ then gives

$$\mu_B = \mu_A^0(T,P) + R\,T \ln x_B + \lambda \frac{n_A^2}{n^2} \qquad (2a)$$

Hence, (1c) gives

$$\left(\frac{\partial \mu_A}{\partial n_A}\right)_{T,P,n_B} = R\,T \frac{1}{x_A} \frac{n_B}{n^2} - 2\,\lambda \frac{n_B^2}{n^3} > 0 \qquad (3)$$

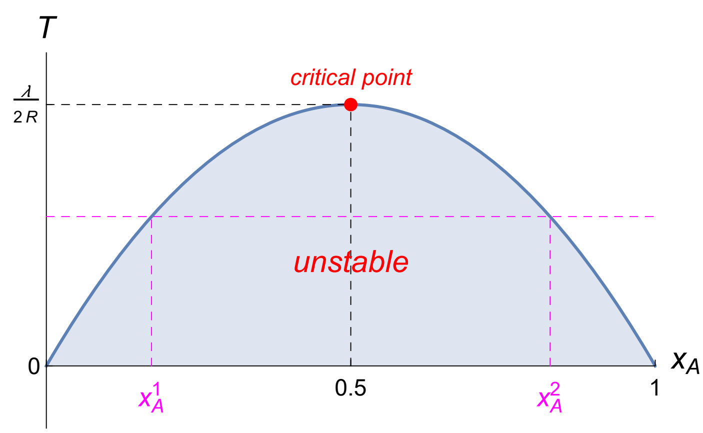
$$\rightarrow \quad R\,T \frac{1}{x_A} - 2\,\lambda\, x_B > 0$$

Thus,

$$\frac{R\,T}{2\,\lambda} > x_A(1 - x_A) \qquad \text{[Stable region.]} \qquad (3a)$$

$$\frac{R\,T}{2\,\lambda} < x_A(1 - x_A) \qquad \text{[Unstable region.]} \qquad (3b)$$

The plot of the stability curve, $\frac{R\,T}{2\,\lambda} = x_A(1 - x_A)$, is given in the figure below, with the unstable region in shades.



For a given $T < \frac{\lambda}{2\,R}$, there are two values of x_A on the coexistence curves. This means there are two stable phases, one with $x_A^1 < 0.5$ and the other $x_A^2 > 0.5$, that can coexist at the same T & P. Although a system point in the shaded area is unstable if the system is in a single phase, it is stable if the system is a mixture of the two coexistent phases so that

$$x_A = c_1\, x_A^1 + c_2\, x_A^2$$

where c_1 & c_2 are the relative concentration of the two phases. The unstable region is therefore also called the coexistent region and the stability curve the coexistence curve.

The critical point at $\left(x_A, \frac{R\,T}{2\,\lambda}\right) = \left(\frac{1}{2}, \frac{1}{4}\right)$ is called critical since for $T > \frac{\lambda}{2\,R}$, there is only 1 stable phase. See Chap 3 for more detailed discussions.

Code

```
Tc = 1/7;
xs = x /. Solve[Tc == x (1 - x), x] // Flatten
```

$$\left\{\frac{1}{14}\left(7-\sqrt{21}\right), \frac{1}{14}\left(7+\sqrt{21}\right)\right\}$$

```
Plot[ x (1 - x), {x, 0, 1}, Filling → Axis,
      AxesLabel → {"x_A", "T"}, TicksStyle → Directive[12],
       Ticks → {{0, 0.5, 1}, {0, {1/4, "λ/(2 R)"}}},
      PlotRange → {{0, 1}, {-.06, .3}},
      Epilog → {Dashed, Line[{{0, 1/4}, {.5, 1/4}}], Line[{{0.5, 0}, {.5, 1/4}}],
         Magenta, Line[{{0, Tc}, {1, Tc}}], Line[{{xs[[1]], 0}, {xs[[1]], Tc}}],
    Text["x_A^1", {xs[[1]], -.03}], Line[{{xs[[2]], 0}, {xs[[2]], Tc}}],
    Text["x_A^2", {xs[[2]], -.03}], Red, PointSize[Large], Point[{.5, 1/4}],
    Text["critical point", {.5, 1.1/4}], Text["unstable", {.5, .5/5}]
   }
  ]
```