

S3.E. Binary Mixtures

Consider a mixture of two fluids 1 & 2. As discussed in §2.F.4, the total Gibbs energy is [see (2.107)]

$$G = G(T, P, n_1, n_2) = \mu_1^1 N_1 + \mu_2^1 N_2 = n_1 \mu_1 + n_2 \mu_2 \quad (3.119)$$

so that [see (2.108)]

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \quad (3.120)$$

The molar version of (3.119) is

$$g = \frac{G}{n} = x_1 \mu_1 + x_2 \mu_2 \quad \left[x_j = \frac{n_j}{n} = \frac{n_j}{n_1 + n_2} \right] \quad (3.121)$$

Meanwhile, writing (3.120) as

$$d(n g) = -n s dT + n v dP + \mu_1 d(n x_1) + \mu_2 d(n x_2)$$

we get

$$n(dg + s dT - v dP - \mu_1 dx_1 - \mu_2 dx_2) + (g - \mu_1 x_1 - \mu_2 x_2) dn = 0$$

With the help of (3.121), we have

$$\begin{aligned} dg &= -s dT + v dP + \mu_1 dx_1 + \mu_2 dx_2 \\ &= -s dT + v dP + (\mu_1 - \mu_2) dx_1 \quad [x_1 + x_2 = 1] \end{aligned} \quad (3.122)$$

so that

$$g = g(T, P, x_1) \quad G = n g = G(T, P, n, x_1) \quad (3.122a)$$

and (3.120) can be written as

$$dG = -SdT + VdP + (\mu_1 - \mu_2) dn_1 + \mu_2 dn_2 \quad (3.122b)$$

Note that (3.122) gives

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P} = \mu_1 - \mu_2 \quad (3.122c)$$

so that

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P} = 0 \quad \Leftrightarrow \quad \mu_1 = \mu_2 \quad (3.122d)$$

which is the familiar condition for chemical equilibrium.

Hence,

$$\begin{aligned} \mu_1 &= \left(\frac{\partial G}{\partial n_1} \right)_{T,P,n_2} && \text{[(3.120) used.]} \\ &= \left(\frac{\partial g}{\partial x_1} \right)_{T,P} + \mu_2 && \text{[(3.122b \& c) used.]} \\ &= \left(\frac{\partial g}{\partial x_1} \right)_{T,P} + \frac{1}{x_2} (g - x_1 \mu_1) && \text{[(3.121) used.]} \\ &= \left(1 + \frac{x_1}{x_2} \right)^{-1} \left[\left(\frac{\partial g}{\partial x_1} \right)_{T,P} + \frac{1}{x_2} g \right] && \text{[} \mu_1 \text{ term moved to LHS.]} \\ &= x_2 \left[\left(\frac{\partial g}{\partial x_1} \right)_{T,P} + \frac{1}{x_2} g \right] && \text{[} x_1 + x_2 = 1 \text{]} \\ &= g + (1 - x_1) \left(\frac{\partial g}{\partial x_1} \right)_{T,P} && \text{(3.123)} \end{aligned}$$

Since switching the particle labels cannot affect the physics, taking $1 \leftrightarrow 2$, then turns (3.123) into

$$\begin{aligned}\mu_2 &= g + (1 - x_2) \left(\frac{\partial g}{\partial x_2} \right)_{T,P} \\ &= g - x_1 \left(\frac{\partial g}{\partial x_1} \right)_{T,P}\end{aligned}\quad (3.124)$$

where use was made of

$$\frac{dx_2}{dx_1} = -1 \quad \rightarrow \quad \frac{\partial}{\partial x_1} = \frac{dx_2}{dx_1} \frac{\partial}{\partial x_2} = - \frac{\partial}{\partial x_2} \quad (3.124a)$$

Taking the derivative of (3.123) gives

$$\left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} = \left(\frac{\partial g}{\partial x_1} \right)_{T,P} - \left(\frac{\partial g}{\partial x_1} \right)_{T,P} + (1 - x_1) \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} = (1 - x_1) \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} \quad (3.126)$$

$$= - \left(\frac{\partial \mu_1}{\partial x_2} \right)_{T,P} = x_2 \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} \quad (3.126a)$$

Taking $1 \leftrightarrow 2$ gives

$$\begin{aligned}\left(\frac{\partial \mu_2}{\partial x_2} \right)_{T,P} &= (1 - x_2) \left(\frac{\partial^2 g}{\partial x_2^2} \right)_{T,P} = x_1 \left(\frac{\partial^2 g}{\partial x_2^2} \right)_{T,P} = x_1 \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} \\ &= - \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,P}\end{aligned}\quad (3.127)$$

Note: Using g is the same as setting $n = 1$ [see (3.122b)].

S3.E.1. Stability Conditions

As discussed in §2.H.2, chemical stability for a system of M species of particles requires the matrix

$$\mathbf{M} = \{ \mu_{i,j} \} = \left\{ \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P, \{ \mu_{k \neq i} \}} \right\} \quad i, j = 1, \dots, M$$

to be symmetric and positive definite, which means every principal minor of \mathbf{M} must be positive definite. For $M = 2$, we have

$$\mu_{1,1} > 0 \quad \mu_{2,2} > 0 \quad \begin{vmatrix} \mu_{1,1} & \mu_{1,2} \\ \mu_{2,1} & \mu_{2,2} \end{vmatrix} > 0 \quad (\mu_{1,2} = \mu_{2,1}) \quad (3.128)$$

Reminder: \mathbf{M} is a positive definite matrix $\Leftrightarrow \mathbf{x}^T \mathbf{M} \mathbf{x} > 0$ for all vector \mathbf{x} .

If \mathbf{M} is also symmetric, then all of its eigenvalues are positive definite.

$d(3.119) - (3.120)$ gives

$$s dT - v dP + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (3.129a)$$

which is the Gibbs-Duhem equation [c.f. (2.62) of §2.E]. Dividing (3.129a) by n gives

$$s dT - v dP + x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad (3.129b)$$

Thus, for processes that keeps T & P constant,

$$n_1 (d\mu_1)_{T,P} + n_2 (d\mu_2)_{T,P} = 0 \quad (3.129)$$

Writing

$$(d\mu_1)_{T,P} = \left(\frac{\partial \mu_1}{\partial n_1} \right)_{T,P,n_2} dn_1 + \left(\frac{\partial \mu_1}{\partial n_2} \right)_{T,P,n_1} dn_2 \quad (3.130)$$

$$= \mu_{1,1} dn_1 + \mu_{1,2} dn_2$$

and

$$\begin{aligned} (d\mu_2)_{T,P} &= \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T,P,n_1} dn_1 + \left(\frac{\partial \mu_2}{\partial n_2} \right)_{T,P,n_1} dn_2 \\ &= \mu_{2,1} dn_1 + \mu_{2,2} dn_2 \end{aligned} \quad (3.131)$$

(3.129) becomes

$$n_1 \mu_{1,1} dn_1 + n_1 \mu_{1,2} dn_2 + n_2 \mu_{2,1} dn_1 + n_2 \mu_{2,2} dn_2 = 0$$

$$\rightarrow (n_1 \mu_{1,1} + n_2 \mu_{2,1}) dn_1 + (n_1 \mu_{1,2} + n_2 \mu_{2,2}) dn_2 = 0 \quad (3.131a)$$

Since dn_1 & dn_2 are independent of each other, (3.131a) can be satisfied only if

$$n_1 \mu_{1,1} + n_2 \mu_{2,1} = 0 \quad \& \quad n_1 \mu_{1,2} + n_2 \mu_{2,2} = 0 \quad (3.131b)$$

i.e.,

$$n_1 \left(\frac{\partial \mu_1}{\partial n_1} \right)_{T,P,n_2} + n_2 \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T,P,n_2} = 0 \quad (3.133)$$

and

$$n_1 \left(\frac{\partial \mu_1}{\partial n_2} \right)_{T,P,n_1} + n_2 \left(\frac{\partial \mu_2}{\partial n_2} \right)_{T,P,n_1} = 0 \quad (3.132)$$

Since $n_j \geq 0$, this means

$$\text{sign}(\mu_{1,1}) = -\text{sign}(\mu_{2,1}) \quad \& \quad \text{sign}(\mu_{1,2}) = -\text{sign}(\mu_{2,2})$$

Owing to the stability conditions (3.128), we have

$$\mu_{1,2} = \mu_{2,1} < 0 \quad (3.134a)$$

Thus, (3.128) can be written as

$$\left(\frac{\partial \mu_1}{\partial n_1} \right)_{T,P,n_2} > 0 \quad \left(\frac{\partial \mu_2}{\partial n_2} \right)_{T,P,n_1} > 0 \quad \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial \mu_1}{\partial n_2} \right)_{T,P,n_1} < 0 \quad (3.134)$$

Using

$$\left(\frac{\partial x_1}{\partial n_1} \right)_{n_2} = \left[\frac{\partial}{\partial n_1} \left(\frac{n_1}{n_1 + n_2} \right) \right]_{n_2} = \frac{1}{n} - \frac{n_1}{n^2} = \frac{n_2}{n^2} = \frac{x_2}{n}$$

we have

$$\mu_{2,1} = \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial x_1}{\partial n_1} \right)_{n_2} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,P} = \frac{x_2}{n} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,P}$$

(3.127) thus becomes

$$\left(\frac{\partial^2 g}{\partial x_2^2} \right)_{T,P} = -\frac{1}{x_1} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,P} = -\frac{n}{x_1 x_2} \mu_{2,1} > 0 \quad (3.135a)$$

Taking $1 \leftrightarrow 2$ gives

$$\left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} = -\frac{n}{x_1 x_2} \mu_{1,2} = \left(\frac{\partial^2 g}{\partial x_2^2} \right)_{T,P} > 0 \quad (3.135)$$

which is to be expected since

$$x_1 + x_2 = 1 \quad \rightarrow \quad \left(\frac{\partial g}{\partial x_1} \right)_{T,P} = -\left(\frac{\partial g}{\partial x_2} \right)_{T,P}$$

Thus, for chemical stability, g must be a convex function of x_j .

S3.E.2. Equilibrium Conditions

As stated in §2.H.2, the equilibrium conditions for chemical equilibrium are

1. $\mu_j = \text{const.}$ in each region accessible to particles of type j .
2. $\mu_j = \mu_k$ if transfer between particles of types j & k is allowed.

This means that for a pair of coexisting phases I & II, in a binary mixture, chemical equilibrium for each type of particles requires

$$\mu_j^I = \mu_j^{II} \quad \forall j = 1, 2 \quad [T < T_c] \quad (3.136)$$

In terms of (3.123-4), these become

$$\mu_1^I = g^I + (1 - x_1^I) \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I = \mu_1^{II} = g^{II} + (1 - x_1^{II}) \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^{II} \quad (3.136)$$

and

$$\mu_2^I = g^I - x_1^I \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I = \mu_2^{II} = g^{II} - x_1^{II} \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^{II} \quad (3.137)$$

(3.136) – (3.137) gives

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I = \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^{II} \quad (3.138)$$

which means the tangents of $g(x_1)$ at the coexisting phases x_1^I & x_1^{II} are equal.

Putting (3.138) back into (3.137) gives

$$\begin{aligned} g^I - x_1^I \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I &= g^{II} - x_1^{II} \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I \\ \rightarrow (x_1^I - x_1^{II}) \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I &= g^I - g^{II} \end{aligned} \quad (3.139)$$

which means that the line joining the tangent points (x_1^I, g^I) & (x_1^{II}, g^{II}) is their common tangent [see Fig.3.35 below].

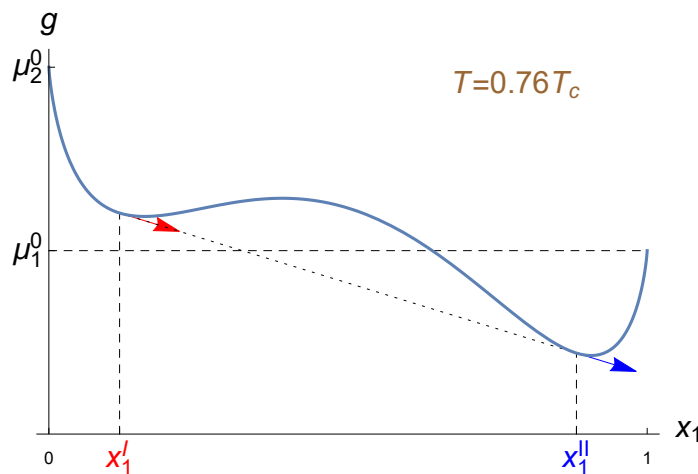


Fig.3.35. Plot of $g(x_1)$ given in Ex.3.6. Tangents (arrows) of g at the coexistence phases x_1^I & x_1^{II} are in the same direction as the (dotted) line joining the tangent points.

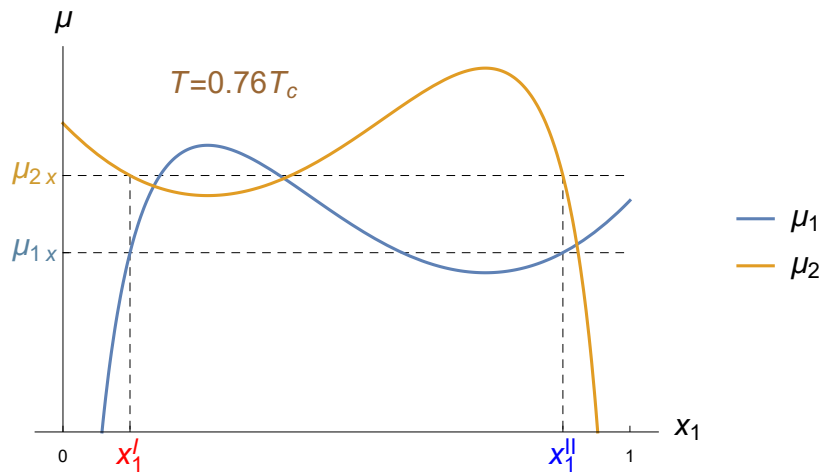


Fig3.35a. Plots of $\mu_1(x_1)$ & $\mu_2(x_1)$ showing compliance of the chemical equilibrium conditions

$$\mu_1^I = \mu_1^{II} = \mu_{1x} \quad \mu_2^I = \mu_2^{II} = \mu_{2x}$$

at the coexisting phases x_1^I & x_1^{II} .

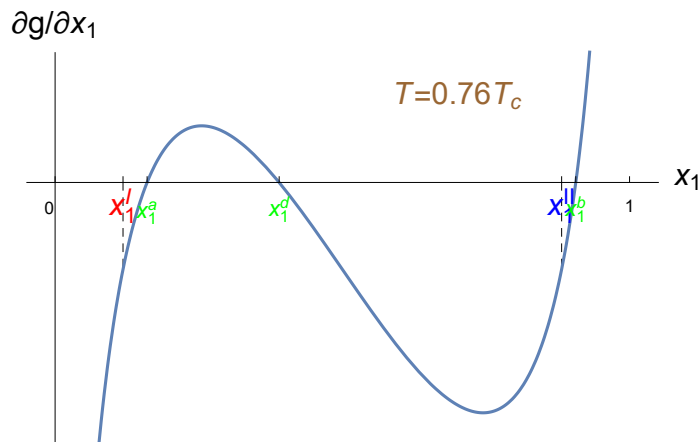


Fig.3.35b. Plot of $\frac{\partial g}{\partial x_1}$ showing that x_1^I & x_1^{II} are close to, but not the minima x_1^a & x_1^b of g .

According to (3.123-4), at an extremum of g ,

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P} = 0 \quad \rightarrow \quad \mu_1 = \mu_2$$

which signifies chemical equilibrium within the single phase there.

Now, on a continuous curve, any two points with the same tangent must be separated by at least 1 minimum and 1 maximum. For the sake of global stability, we also have

$$G \rightarrow \infty \quad \text{as} \quad n_j \rightarrow \infty$$

Combining these two requirements means that $g(x_1)$ must have at least 2 minima separated by 1 maximum [c.f. Fig.3.35]. Therefore,

$$\frac{\partial g}{\partial x_1} = A (x_1 - x_1^a) (x_1 - x_1^b) (x_1 - x_1^c)$$

where $x_1^a = x_1^a(T, P)$ denote the extrema and A is some function of (T, P, x_1) that has no real roots.

At the critical point C , all 3 extrema coalesce into one minimum so that

$$\frac{\partial g}{\partial x_1} = A (x_1 - x_1^c)^3 \quad [x_1^a(T_c, P_c) = x_1^b(T_c, P_c) = x_1^c(T_c, P_c) = x_1^c]$$

Taking the derivatives (at fixed T & P) gives

$$\begin{aligned} \frac{\partial^2 g}{\partial x_1^2} &= \frac{\partial A}{\partial x_1} (x_1 - x_1^c)^3 + 3A (x_1 - x_1^c)^2 \\ \frac{\partial^3 g}{\partial x_1^3} &= \frac{\partial^2 A}{\partial x_1^2} (x_1 - x_1^c)^3 + 6 \frac{\partial A}{\partial x_1} (x_1 - x_1^c)^2 + 6A (x_1 - x_1^c) \end{aligned}$$

The conditions for the critical point C are therefore,

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P}^c = \left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P}^c = \left(\frac{\partial^3 g}{\partial x_1^3} \right)_{T,P}^c = 0 \quad (3.139a)$$

Ex.3.6.

Consider the following model Gibbs free energy for a binary mixture [c.f. (2.243) of §S2.D.1]

$$G = n_1 [\mu_1^0(T, P) + RT \ln x_1] + n_2 [\mu_2^0(T, P) + RT \ln x_2] + \lambda n x_1 x_2 \quad (0a)$$

where

$$\begin{aligned} n &= n_1 + n_2 \\ \mu_j^0(T, P) &= \frac{G}{n} \Big|_{x_j=1} \quad x_j = \frac{n_j}{n} \quad j = 1, 2 \end{aligned} \quad (0b)$$

(a) Plot the molar Gibbs energy g vs x_1 assuming

$$\mu_1^0 = 1.0 \quad \mu_2^0 = 1.05 \quad RT = 0.38 \quad \lambda = 1 \quad (0c)$$

Find x_1^I & x_2^{II} .

(b) Use the conditions [see (3.139j)]

$$\left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P}^c = \left(\frac{\partial^3 g}{\partial x_1^3} \right)_{T,P}^c = 0 \quad (0d)$$

to find the critical point C .

(c) Demonstrate explicitly that the equilibrium conditions

$$\mu_1^I = \mu_1^{II} \quad \& \quad \mu_2^I = \mu_2^{II}$$

are equivalent to the condition

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P}^I = \left(\frac{\partial g}{\partial x_1} \right)_{T,P}^{II} \quad (0e)$$

(d) Find the coexistence region in the x_1 - T plane.

Answer (a)

The molar Gibbs energy is given by (0a) as

$$\begin{aligned}
 g &= \frac{G}{n} = x_1 [\mu_1^0(T, P) + RT \ln x_1] + x_2 [\mu_2^0(T, P) + RT \ln x_2] + \lambda x_1 x_2 \\
 &= x_1 [\mu_1^0(T, P) + RT \ln x_1] + (1 - x_1) [\mu_2^0(T, P) + RT \ln (1 - x_1)] + \lambda x_1 (1 - x_1)
 \end{aligned} \tag{1}$$

The extrema of g are the solutions to

$$\begin{aligned}
 \frac{\partial g}{\partial x_1} &= \mu_1^0 + RT \ln x_1 + RT - \mu_2^0 - RT \ln (1 - x_1) - RT + \lambda (1 - 2x_1) \\
 &= \mu_1^0 - \mu_2^0 + RT \ln \frac{x_1}{1 - x_1} + \lambda (1 - 2x_1) = 0
 \end{aligned} \tag{1a}$$

which can only be solved numerically [see §Code (a)].

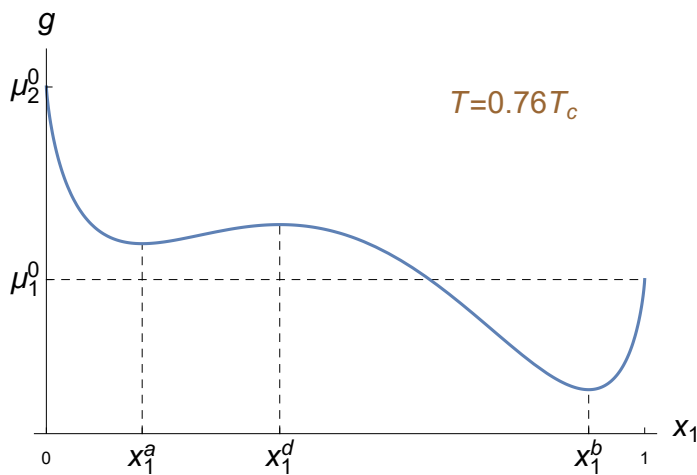


Fig.3.37a. Plot of $g(x_1)$ for

$$\begin{array}{llll}
 \mu_1^0 = 1.0 & \mu_2^0 = 1.05 & RT = 0.38 & \lambda = 1 \\
 \text{Extrema are at} & & & \\
 x_1^a = 0.16 & x_1^d = 0.39 & x_1^b = 0.90 &
 \end{array}$$

Code (a)

```

In[ ]:= g = x1 (μ1θ + R T Log [x1]) + x2 (μ2θ + R T Log [x2]) + λ x1 x2;

In[ ]:= par = {μ1θ → 1.0, μ2θ → 1.05, T → 0.38 / R, λ → 1, x2 → 1 - x1};

In[ ]:= gp = g /. par // Simplify;
pdg = ∂x1 gp;
sol = NSolve[pdg == 0, x1, Reals];
xs = x1 /. sol;
gxs = gp /. sol;

In[ ]:= (* extrema location *)
xs

```

```

In[ ]:= (* Fig.37a: Plot of g(x1) *)
tic =
  {{0, {xs[[1]], "x1a"}, {xs[[2]], "x1d"}, {xs[[3]], "x1b"}, 1}, {{μ10, "μ10"}, {μ20, "μ20"}} /. par};
gm = .96;
Plot[gp, {x1, 0, 1},
  PlotRange → {All, {gm, 1.06}},
  AxesLabel → {"X1", "g"}, AxesOrigin → {0, gm},
  Ticks → tic,
  Prolog → {Dashed, Line[{{xs[[1]], gm}, {xs[[1]], gxs[[1]]}],
  Line[{{xs[[2]], gm}, {xs[[2]], gxs[[2]]}], Line[{{xs[[3]], gm}, {xs[[3]], gxs[[3]]}],
  Line[{{0, μ10}, {1, μ10}} /. par], Text["T=0.76Tc", .78 {1, 1.34 μ10} /. par]
  }
]

```

Answer (b)

Differentiating (1a) gives the conditions for the critical point as

$$\begin{aligned}
 \frac{\partial^2 g}{\partial x_1^2} &= RT \left(\frac{1}{x_1} + \frac{1}{1-x_1} \right) - 2\lambda \\
 &= \frac{RT}{x_1(1-x_1)} - 2\lambda = 0 \qquad \qquad \qquad [(3.139i) \text{ used.}] \qquad (1b)
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{\partial^3 g}{\partial x_1^3} &= RT \left[-\frac{1}{x_1^2(1-x_1)} + \frac{1}{x_1(1-x_1)^2} \right] \\
 &= RT \left[-\frac{1-2x_1}{x_1^2(1-x_1)^2} \right] = 0 \qquad \qquad \qquad (1c)
 \end{aligned}$$

(1c) gives

$$x_1^c = \frac{1}{2} \qquad \qquad \qquad (1d)$$

so that (1b) gives

$$RT_c = \frac{\lambda}{2} \qquad \qquad \qquad (1e)$$

Putting these back into (1) gives

$$g^c = \frac{1}{2} (\mu_1^{0c} + \mu_2^{0c}) + \frac{1}{4} \lambda (1 - 2 \ln 2)$$

where

$$\mu_j^{0c} = \mu_j^0(T_c, P_c)$$

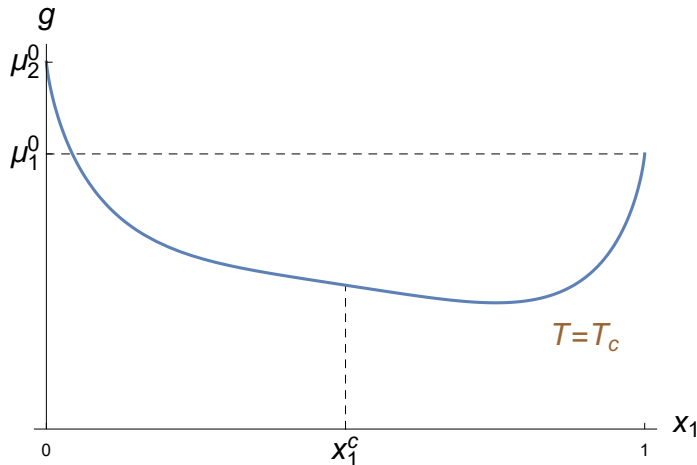


Fig.3.37b. Molar Gibbs function $g(x_1)$ at the critical temperature $RT_c = \frac{\lambda}{2}$, with

$$\mu_1^0 = 1.0 \quad \mu_2^0 = 1.05 \quad \lambda = 1$$

Using the dimensionless quantities

$$\bar{T} = \frac{T}{T_c} = \frac{2RT}{\lambda} \quad \bar{g} = \frac{g}{RT_c} = \frac{2g}{\lambda} \quad \bar{\mu}_j^0 = \frac{\mu_j^0}{RT_c} = \frac{2\mu_j^0}{\lambda} \quad (1f)$$

we can write (1) as

$$\bar{g} = x_1 (\bar{\mu}_1^0 + \bar{T} \ln x_1) + (1 - x_1) [\bar{\mu}_2^0 + \bar{T} \ln (1 - x_1)] + 2x_1(1 - x_1) \quad (1g)$$

so that (1a) becomes

$$\frac{\partial \bar{g}}{\partial x_1} = \bar{\mu}_1^0 - \bar{\mu}_2^0 + \bar{T} \ln \frac{x_1}{1 - x_1} + 2(1 - 2x_1) \quad (1h)$$

Code (b)

```
ln[ ]:= (g /. x2 -> 1 - x1) /. {x1 -> 1/2, T -> lambda/(2R) Tb} // Simplify

ln[ ]:= g3 = D[g2, x1] // Simplify

ln[ ]:= Solve[g3 == 0, x1]

ln[ ]:= g = x1 (mu10 + R T Log[x1]) + x2 (mu20 + R T Log[x2]) + lambda x1 x2;

ln[ ]:= par = {mu10 -> 1.0, mu20 -> 1.05, T -> 0.5/R, lambda -> 1, x2 -> 1 - x1};
gc = g /. par // Simplify;

ln[ ]:= tic = {{0, {0.5, "x1^c"}, 1}, {{mu10, "mu1^0"}, {mu20, "mu2^0"}} /. par};
gm = .85;
gb = g /. par /. x1 -> .5
```

```

In[ ]:= (* Fig.37b: Plot of g(x1) at T=Tc *)
Plot[gc, {x1, 0, 1},
  PlotRange → {All, {gm, 1.06}},
  AxesLabel → {"X1", "g"}, AxesOrigin → {0, gm},
  Ticks → tic,
  Prolog → {Dashed, Line[{{.5, gm}, {.5, gb}}]},
  Line[{{0, μ10}, {1, μ10}} /. parc], Text["T=Tc", .9 {1, μ10} /. parc]
]

```

Answer (c)

Using (0a) and

$$\begin{aligned} \left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} &= \left[\frac{\partial}{\partial n_1} \left(\frac{n_1}{n_1 + n_2}\right)\right]_{n_2} = \frac{1}{n} - \frac{n_1}{n^2} = \frac{n_2}{n^2} = \frac{x_2}{n} \\ \left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} &= \left[\frac{\partial}{\partial n_1} \left(\frac{n_2}{n_1 + n_2}\right)\right]_{n_2} = -\frac{n_2}{n^2} = -\frac{x_2}{n} \\ \left(\frac{\partial x_2}{\partial n_2}\right)_{n_1} &= \frac{x_2}{n} & \left(\frac{\partial x_1}{\partial n_2}\right)_{n_1} &= -\frac{x_1}{n} \end{aligned} \quad [1 \leftrightarrow 2 \text{ of above results.}]$$

we have

$$\begin{aligned} \mu_1 &= \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \mu_1^0 + RT \ln x_1 + n_1 RT \frac{x_2}{x_1 n} - n_2 RT \frac{x_2}{x_2 n} + \lambda \left(x_1 x_2 + n \frac{x_2}{n} x_2 - n x_1 \frac{x_2}{n}\right) \\ &= \mu_1^0 + RT \ln x_1 + \lambda x_2^2 \end{aligned} \quad (2a)$$

1 ↔ 2 on (2a) gives

$$\mu_2 = \mu_2^0 + RT \ln x_2 + \lambda x_1^2 \quad (2)$$

Hence, the conditions

$$\mu_1^I = \mu_1^{II} \quad \& \quad \mu_2^I = \mu_2^{II}$$

give

$$RT \ln x_1^I + \lambda (1 - x_1^I)^2 = RT \ln x_1^{II} + \lambda (1 - x_1^{II})^2 \quad (4)$$

&

$$RT \ln (1 - x_1^I) + \lambda (x_1^I)^2 = RT \ln (1 - x_1^{II}) + \lambda (x_1^{II})^2 \quad (5)$$

On the other hand, using (1a) turns the condition

$$\left(\frac{\partial g}{\partial x_1}\right)_{T,P}^I = \left(\frac{\partial g}{\partial x_1}\right)_{T,P}^{II}$$

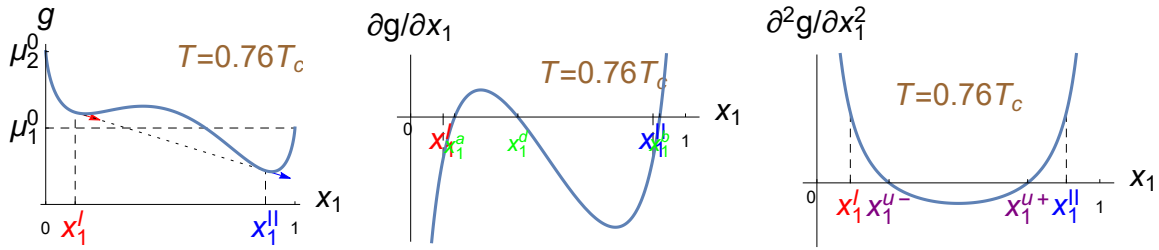
into

$$RT \ln \frac{x_1^I}{1 - x_1^I} + \lambda (1 - 2x_1^I) = RT \ln \frac{x_1^{II}}{1 - x_1^{II}} + \lambda (1 - 2x_1^{II}) \quad (3)$$

which is simply (4) – (5). Hence, the two sets of conditions are equivalent.

Answer (d)

We start by examining g & its derivatives for $T < T_c$ as shown in the following figures.



The $\frac{\partial^2 g}{\partial x_1^2}$ graph shows

$$\frac{\partial^2 g}{\partial x_1^2} < 0 \quad \text{for} \quad x_1 \in (x_1^{u-}, x_1^{u+})$$

which, according to (3.135), indicates chemical instability.

Using (1b), we have

$$\frac{\partial^2 g}{\partial x_1^2} = \frac{RT}{x_1(1-x_1)} - 2\lambda = 0 \quad \text{or} \quad \frac{\bar{T}}{x_1(1-x_1)} - 4 = 0$$

Hence,

$$x_1^{u\pm} = \frac{1}{2} \left(1 \pm \sqrt{1 - \bar{T}} \right) \tag{6}$$

defines the boundary of chemical (in)stability.

The coexistence region is shown in Fig.3.36 below.

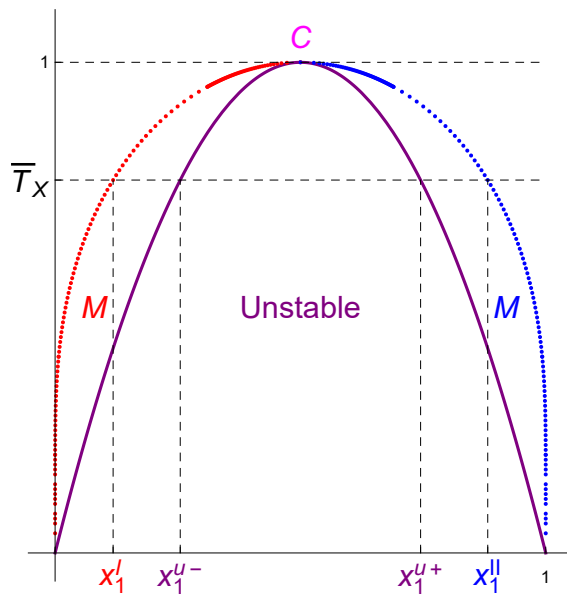


Fig.3.36. Coexistence region for $\mu_1^0 = 1.0$ and $\mu_2^0 = 1.05$.

Red & Blue dots are numerical results for the coexisting phases x_1^I & x_1^{II} , respectively.

Sample points are given at transition temperature $\bar{T}_X = 0.76$.

The purple curve is the border, $\frac{\partial^2 g}{\partial x_1^2} = 0$, between chemically stable and unstable regions.

Regions marked by *M* & *M* are metastable because,

$$\frac{\partial g^\alpha}{\partial x_1} \neq 0 \quad \rightarrow \quad \mu_1^\alpha \neq \mu_2^\alpha \quad \forall \alpha = I, II$$

so that chemical equilibrium is not established within each of the two coexisting phases.

Code (d)

Only reduced quantities are used in this section.

```

In[ ]:= Clear["Global`*"]

In[ ]:= g[x1_, T_, μ10_, μ20_] := x1 (μ10 + T Log[x1]) + (1 - x1) (μ20 + T Log[1 - x1]) + 2 x1 (1 - x1)

In[ ]:= (* extrema of g *)
{T, μ10, μ20} = {.76, 2, 2.1};
gp = g[x1, T, μ10, μ20]
pdg = ∂x1 gp;
sol = NSolve[pdg == 0, x1, Reals];
xs = x1 /. sol;
gxs = gp /. sol

Out[ ]:= 2 (1 - x1) x1 + (1 - x1) (2.1 + 0.76 Log[1 - x1]) + x1 (2 + 0.76 Log[x1])

Out[ ]:= {2.01865, 2.02855, 1.94284}

In[ ]:= (* x1± *)
ppdg = ∂x1 pdg;
xps1 = x1 /. NSolve[ppdg == 0, x1, Reals]

Out[ ]:= {0.255051, 0.744949}

In[ ]:= {1/2 (1 - √(1 - T)), 1/2 (1 + √(1 - T))}

Out[ ]:= {0.255051, 0.744949}

(x'1 - x''1) (∂g/∂x1)T,P = g' - g''

In[ ]:= xcoex[T_, μ10_, μ20_, {xI0_, xII0_}] := Module[{xI, gI, pdgI, xII, gII, pdgII},
  gI = g[xI, T, μ10, μ20];
  pdgI = ∂xI gI // Simplify;
  gII = g[xII, T, μ10, μ20];
  pdgII = ∂xII gII // Simplify;
  {xI, xII} /. FindRoot[{pdgI == pdgII, (xI - xII) pdgI == gI - gII}, {{xI, xI0}, {xII, xII0}}]
]

In[ ]:= xco = xcoex[T, μ10, μ20, {.1, .9}]

Out[ ]:= {0.118226, 0.881774}

In[ ]:= gco = gp /. x1 → xco

Out[ ]:= {2.02051, 1.94415}

```

```
In[ ]:= pdgco = pdg /. x1 → xco
```

```
Out[ ]:= {-0.1, -0.1}
```

```
In[ ]:= (* Fig.37a: Plot of  $g(x_1)$  *)
```

```
ticx = {0, {xco[[1]], "x1I"}, {xco[[2]], "x1II"}, 1};
tic = {ticx, {{μ10, "μ10"}, {μ20, "μ20"}}};
gm = 1.9; Δx = .1; color = {Red, Blue};
Plot[gp, {x1, 0, 1},
  PlotRange → {All, {gm, 2.11}},
  AxesLabel → {"X1", "g"}, AxesOrigin → {0, gm},
  Ticks → tic,
  Prolog → {Table[
    {color[[i]], Arrow[{{xco[[i]], gco[[i]], {xco[[i]] + Δx, gco[[i]] + Δx pdgco[[i]]}}]}, {i, 2}],
  Dotted, Line[{{xco[[1]], gco[[1]], {xco[[2]], gco[[2]]}},
  Dashed, Line[{{0, μ10}, {1, μ10}}],
  Table[
    Line[{{xco[[i]], gm}, {xco[[i]], gco[[i]]}], {i, 2}],
  Text["T=0.76Tc", .78 {1, 1.34 μ10}
  ]
]
```

```
(* Fig.3.35a *)
```

```
μ1 = gp + (1 - x1) pdg;
μ2 = gp - x1 pdg;
μ1x = μ1 /. x1 → xco[[1]];
μ2x = μ2 /. x1 → xco[[2]];
ticμ = {{μ1x, "μ1x"}, {μ2x, "μ2x"}}};
Plot[{μ1, μ2}, {x1, 0, 1},
  PlotRange → {{-.05, 1.051}, {1.7, 2.2}}, AxesOrigin → {0, 1.7},
  AxesLabel → {"X1", "μ"},
  Ticks → {ticx, ticμ},
  PlotLegends → {"μ1", "μ2"},
  Prolog → {Dashed, Line[{{0, μ1x}, {1, μ1x}}], Line[{{0, μ2x}, {1, μ2x}}],
  Line[{{xco[[1]], 0}, {xco[[1]], μ2x}], Line[{{xco[[2]], 0}, {xco[[2]], μ2x}],
  Text["T=0.76Tc", {.3, 2.15}
  ]
]
```

```
In[ ]:= x1m = x1 /. NSolve[pdg == 0, x1, Reals]
```

```
Out[ ]:= {0.160153, 0.390053, 0.906412}
```

```
In[ ]:= x1mT = {"x1a", "x1d", "x1b"};
```

```
In[ ]:= ticm = Table[{x1m[[i]], x1mT[[i]]}, {i, 3}];
```

```
ticp = {ticx ∪ ticm, None}
```

```
Out[ ]:= {{0, 1, {0.118226, x1I}, {0.160153, x1a},
  {0.390053, x1d}, {0.881774, x1II}, {0.906412, x1b}}, None}
```

```
(* Fig.3.35b,  $\frac{\partial g}{\partial x_1}$  *)
Plot[pgd, {x1, 0, 1},
  PlotRange -> {{-.05, 1.051}, .15 {-2, 1}}, AxesOrigin -> {0, 0},
  AxesLabel -> {"X1", "∂g/∂X1"}, Ticks -> ticp,
  Prolog -> {Dashed, Table[
    Line[{{xco[[i]], 0}, {xco[[i]], pdg /. x1 -> xco[[i]]}], {i, 2}],
  Text["T=0.76Tc", {.7, .1}], Text["0", {- .01, - .03}],
  Opacity[.15], Red, Rectangle[{xco[[2]], pdg /. x1 -> xco[[2]], {xco[[1]], pdg /. x1 -> xco[[1]]}]
  ]
]

In[ ]:= tic2 = {{xps1[[1]], "x1u-"}, {xps1[[2]], "x1u+"}};

In[ ]:= (*  $\frac{\partial^2 g}{\partial x_1^2}$  *)
Plot[ppdg, {x1, 0, 1},
  PlotRange -> {{-.05, 1.051}, 6 {- .5, 1}}, AxesOrigin -> {0, 0},
  AxesLabel -> {"X1", "∂2g/∂X12"}, Ticks -> {ticx ∪ tic2, None},
  Prolog -> {Dashed, Table[
    Line[{{xco[[i]], 0}, {xco[[i]], ppgd /. x1 -> xco[[i]]}], {i, 2}],
  Text["T=0.76Tc", {.5, 4}], Text["0", {- .02, - .7}]]]

In[ ]:= xg20[T_] := { $\frac{1}{2} (1 - \sqrt{1-T})$ ,  $\frac{1}{2} (1 + \sqrt{1-T})$ }

In[ ]:= lxun = ParametricPlot[ {#, T} & /@ xg20[T], {T, 0, 1}, PlotStyle -> Purple];

In[ ]:= xcoex[0.045, μ10, μ20, {0.01, .995}] // Chop

... FindRoot: The line search decreased the step size to within tolerance specified by AccuracyGoal and PrecisionGoal but was
unable to find a sufficient decrease in the merit function. You may need more than MachinePrecision digits of working
precision to meet these tolerances.

Out[ ]:= {0, 1.}
```

Due to numerical instability, data points for the coexistence curve must be done in multiple segments of different initial points. Function “Chop” is used to eliminate small imaginary parts in the solutions due to numerical error.

```
In[ ]:= dat1 = Table[{#, T} & /@ xcoex[T, μ10, μ20, {.1, .9}], {T, 0.4, .95, .01}];
dat2 = Table[{#, T} & /@ xcoex[T, μ10, μ20, {.35, .65}], {T, 0.95, .994, .001}];
dat3 = Table[{#, T} & /@ xcoex[T, μ10, μ20, {.45, .55}], {T, 0.995, 1, .001}];
dat4 = Table[{#, T} & /@ xcoex[T, μ10, μ20, {0.05, .95}] // Chop, {T, 0.2, .4, .01}];
dat5 = Table[{#, T} & /@ xcoex[T, μ10, μ20, {0.01, .995}] // Chop, {T, 0.04, .2, .01}];
dat = (dat1 ∪ dat2 ∪ dat3 ∪ dat4 ∪ dat5)T;

(* coexistence curve *)
lco = ListPlot[dat, PlotStyle -> {Red, Blue}]
```

```
(* adornments *)
gr = Graphics[{Dashed, Line[{{0, T}, {1, T}], Line[{{0, 1}, {1, 1}]},
  Table[Line[{{xco[[i], 0}, {xco[[i], T}], {i, 2}],
  Table[Line[{{xg20[T][i], 0}, {xg20[T][i], T}], {i, 2}],
  Text["Unstable", {.5, .5}], Text["M", {.08, .5}], Text["M", {.92, .5}],
  Text["C", {.5, 1.05}]
}]

(* Fig.3.36 *)
Show[{lxun, lco, gr}, PlotRange -> All,
  Ticks -> {ticx ∪ tic2, {{T, "T̄x"}, 1}}]
```

S3.E.3. Coexistence Curve

Partial molar quantities are defined as

$$f_j \equiv \frac{\partial F}{\partial n_j} \quad (3.140a)$$

For the Gibbs energy

$$G = U - TS + PV = \sum_{j=1}^M n_j \mu_j \quad (3.140b)$$

we have

$$\begin{aligned} \mu_j &= \left(\frac{\partial G}{\partial n_j} \right)_{T, P, \{n_{k \neq j}\}} && j, k = 1, \dots, M \\ &= \left(\frac{\partial U}{\partial n_j} \right)_{T, P, \{n_{k \neq j}\}} - T \left(\frac{\partial S}{\partial n_j} \right)_{T, P, \{n_{k \neq j}\}} + P \left(\frac{\partial V}{\partial n_j} \right)_{T, P, \{n_{k \neq j}\}} && [(3.140b) \text{ used.}] \quad (3.140) \end{aligned}$$

$$= u_j - T s_j + P v_j \quad [(3.140a) \text{ used.}] \quad (3.141)$$

Using

$$n = \sum_{j=1}^M n_j \quad \rightarrow \quad \frac{\partial n}{\partial n_j} = 1$$

the relation between molar & partial molar quantities is easily derived from (3.140a) as

$$f_j = \frac{\partial (nf)}{\partial n_j} = f + n \frac{\partial f}{\partial n_j} \quad [f \equiv \frac{F}{n}] \quad (3.142a)$$

Now, (3.139d) can be generalized to

$$\left(\frac{\partial x_j}{\partial n_j} \right)_{\{n_{k \neq j}\}} = \left[\frac{\partial}{\partial n_j} \left(\frac{n_j}{n} \right) \right]_{\{n_{k \neq j}\}} = \frac{1}{n} - \frac{n_j}{n^2} = \frac{n - n_j}{n^2} = \frac{1 - x_j}{n}$$

and for $k \neq j$,

$$\left(\frac{\partial x_k}{\partial n_j} \right)_{\{n_{m \neq j, k}\}} = \left[\frac{\partial}{\partial n_j} \left(\frac{n_k}{n} \right) \right]_{\{n_{m \neq j, k}\}} = -\frac{n_k}{n^2} = -\frac{x_k}{n}$$

so that, combining the two results,

$$\frac{\partial x_k}{\partial n_j} = \frac{\delta_{jk} - x_k}{n} \quad (3.142b)$$

Using

$$n_j = n x_j = x_j \sum_k n_k = \frac{x_j}{1 - x_j} \sum_{k \neq j} n_k$$

we see that n_j depends only on x_j if we keep all $n_{k \neq j}$ constant. Hence,

$$\left(\frac{\partial f}{\partial n_j} \right)_{\{n_{k \neq j}\}} = \left(\frac{\partial x_j}{\partial n_j} \right)_{\{n_{m \neq j, k}\}} \frac{\partial f}{\partial x_j} = \frac{1-x_j}{n} \frac{\partial f}{\partial x_j} \quad [(3.142b) \text{ used. }] \quad (3.142c)$$

(3.142a) thus becomes

$$f_j = f + (1-x_j) \frac{\partial f}{\partial x_j} \quad (3.142d)$$

In particular, for $M=2$,

$$v_1 = v + (1-x_1) \left(\frac{\partial v}{\partial x_1} \right)_{T,P} \quad (3.142)$$

For the enthalpy

$$H = U + PV$$

the partial molar enthalpies are

$$h_j = \left(\frac{\partial H}{\partial n_j} \right)_{T,P,\{n_{k \neq j}\}} = u_j + P v_j \quad (3.143)$$

Comparing (3.143) with (3.141) gives

$$\mu_j = h_j - T s_j \quad (3.143a)$$

Back to the problem of the binary mixture, the conditions for the coexistence curve are

$$\mu_j^I = \mu_j^{II} \quad j = 1, 2$$

where

$$\mu_j = \mu_j(T, P, n_1, n_2) = \mu_j(T, P, x_1)$$

Thus, if one moves along the coexistence curve so that

$$d T^I = d T^{II} \equiv d T \quad d P^I = d P^{II} \equiv d P$$

then

$$d \mu_j^I = d \mu_j^{II} \quad (3.143b)$$

Reminder: the coexistence region Γ_{coex} is now a 3-D manifold in the 5-D space $\Gamma = (T, P, v, \mu_1, x_1)$. The coexistence curves are the projections of the 2-D boundary of Γ_{coex} onto some 2-D plane in Γ .

We are interested in the coexistence curve in the x_1 - T plane, i.e., we wish to find

$$x_1^\alpha(T, P) \quad \forall T \leq T_c \quad \& \quad \alpha = I, II$$

or, equivalently, the differential equations obeyed by them. Obviously, an auxiliary condition on P is needed to make the projection unique.

To this end, we make use of (3.143b) and consider the differential $d\left(\frac{\mu_j}{T}\right)$. Taking $\mu_j = \mu_j(T, P, n_1, n_2)$, we

have

$$\begin{aligned} d\left(\frac{\mu_j^\alpha}{T}\right) &= \left[\frac{\partial}{\partial T} \left(\frac{\mu_j^\alpha}{T} \right) \right]_{P, n_1^\alpha, n_2^\alpha} dT + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial P} \right)_{T, n_1^\alpha, n_2^\alpha} dP \\ &\quad + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial n_1^\alpha} \right)_{T, P, n_2} d n_1^\alpha + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial n_2^\alpha} \right)_{T, P, n_1} d n_2^\alpha \end{aligned} \quad (3.144)$$

Using the Maxwell relations (2.113-4) of §2.F.4

$$\left(\frac{\partial \mu_j}{\partial T} \right)_{P, n_1, n_2} = - \left(\frac{\partial S}{\partial n_j} \right)_{T, P, n_{k \neq j}} \quad \left(\frac{\partial \mu_j}{\partial P} \right)_{T, n_1, n_2} = \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_{k \neq j}}$$

we get

$$\left[\frac{\partial}{\partial T} \left(\frac{\mu_j^\alpha}{T} \right) \right]_{P, n_1^\alpha, n_2^\alpha} = -\frac{\mu_j^\alpha}{T^2} - \frac{1}{T} \left(\frac{\partial S^\alpha}{\partial n_j^\alpha} \right)_{T, P, n_{k \neq j}^\alpha} = -\frac{\mu_j^\alpha}{T^2} - \frac{s_j^\alpha}{T} = -\frac{h_j^\alpha}{T^2}$$

$$\left(\frac{\partial \mu_j^\alpha}{\partial P} \right)_{T, n_1, n_2} = v_j^\alpha$$

so that (3.144) becomes

$$d \left(\frac{\mu_j^\alpha}{T} \right) = -\frac{h_j^\alpha}{T^2} dT + \frac{v_j^\alpha}{T} dP + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial n_1^\alpha} \right)_{T, P, n_2} d n_1^\alpha + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial n_2^\alpha} \right)_{T, P, n_1} d n_2^\alpha$$

or

$$d \left(\frac{\mu_j^\alpha}{T} \right) = -\frac{h_j^\alpha}{T^2} dT + \frac{v_j^\alpha}{T} dP + \frac{1}{T} \left(\frac{\partial \mu_j^\alpha}{\partial x_1^\alpha} \right)_{T, P} d x_1^\alpha \quad j = 1, 2 \quad (3.146-7)$$

where we have used

$$\begin{aligned} (d \mu_j)_{T, P} &= \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P} d x_1 && [\mu_j = \mu_j(T, P, x_1)] \\ &= \left(\frac{\partial \mu_j}{\partial n_1} \right)_{T, P, n_2} d n_1 + \left(\frac{\partial \mu_j}{\partial n_2} \right)_{T, P, n_1} d n_2 && [\mu_j = \mu_j(T, P, n_1, n_2)] \end{aligned}$$

Now, (3.143b) implies

$$d \left(\frac{\mu_j^I}{T} \right) = d \left(\frac{\mu_j^{II}}{T} \right)$$

so that (3.146-7) give

$$0 = -\frac{h_j^I - h_j^{II}}{T^2} dT + \frac{v_j^I - v_j^{II}}{T} dP + \frac{1}{T} \left[\left(\frac{\partial \mu_j^I}{\partial x_1^I} \right)_{T, P} d x_1^I - \left(\frac{\partial \mu_j^{II}}{\partial x_1^{II}} \right)_{T, P} d x_1^{II} \right]$$

which, with

$$\Delta f \equiv f^I - f^{II} \quad \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P}^\alpha \equiv \left(\frac{\partial \mu_j^\alpha}{\partial x_1^\alpha} \right)_{T, P}$$

can be written as

$$-\frac{\Delta h_j}{T} dT + \Delta v_j dP + \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P}^I d x_1^I - \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P}^{II} d x_1^{II} = 0 \quad j = 1, 2 \quad (3.148-9)$$

For isobar processes, $P = \text{const}$, and (3.148-9) reduce to

$$-\frac{\Delta h_j}{T} + \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P}^I \left(\frac{d x_1^I}{dT} \right)_P - \left(\frac{\partial \mu_j}{\partial x_1} \right)_{T, P}^{II} \left(\frac{d x_1^{II}}{dT} \right)_P = 0 \quad j = 1, 2 \quad (3.150-1)$$

or

$$\begin{pmatrix} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T, P}^I & - \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T, P}^{II} \\ \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, P}^I & - \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, P}^{II} \end{pmatrix} \begin{pmatrix} \left(\frac{d x_1^I}{dT} \right)_P \\ \left(\frac{d x_1^{II}}{dT} \right)_P \end{pmatrix} = \begin{pmatrix} \frac{\Delta h_1}{T} \\ \frac{\Delta h_2}{T} \end{pmatrix}$$

where $\left(\frac{\partial \mu_j}{\partial x_j} \right)_{T, P}^\alpha$ can be written in terms of $\left(\frac{\partial^2 g}{\partial x_j^2} \right)_{T, P}^\alpha$ using (3.126-7).

Using *Mathematica* to do the dirty work, we have [see §Code]

$$\left(\frac{dx_1^I}{dT}\right)_P = \frac{x_1^I \Delta h_1 - (1 - x_1^I) \Delta h_2}{T(x_1^I - x_1^II) \left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,P}^I} \quad (3.152)$$

$$\left(\frac{dx_1^II}{dT}\right)_P = \frac{x_1^II \Delta h_1 + (1 - x_1^II) \Delta h_2}{T(x_1^I - x_1^II) \left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,P}^{II}} \quad (3.153)$$

Code

```
In[*]:= Clear["Global`*"]
```

```
In[*]:= xs = {x, y} /. Solve[{a x + b y == A, c x + d y == B}, {x, y}] // Flatten
```

```
Out[*]:= { - (b B + A d) / (b c - a d), - (a B - A c) / (b c - a d) }
```

```
In[*]:= par = {a -> (1 - xI) g2I, b -> - (1 - xII) g2II, c -> -xI g2I, d -> xII g2II, A -> h1/T, B -> h2/T};
```

```
(* (3.152-3) *)
```

```
xs /. par // Simplify // Factor
```

```
Out[*]:= { - (h2 - h1 xII + h2 xII) / (g2I T (-xI + xII)), - (h2 - h1 xI + h2 xI) / (g2II T (xI - xII)) }
```

```
In[*]:= a d - b c /. par // Simplify // Factor
```

```
Out[*]:= -g2I g2II (xI - xII)
```

```
In[*]:= A d - B b /. par // Simplify // Factor
```

```
Out[*]:= - (g2II (-h2 - h1 xII + h2 xII)) / T
```

```
In[*]:= a B - A c /. par // Simplify // Factor
```

```
Out[*]:= - (g2I (-h2 - h1 xI + h2 xI)) / T
```