Solution 8.1

Hooke's law for an isotropic linear elastic deformation is given by

$$\sigma_{ij} = 2\mu\epsilon_{ij} + \lambda\delta_{ij}\sum_{i=1}^{i=3}\epsilon_{ii} \tag{1}$$

where $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$. This equation is the component form of the matrix equation in the Lecture Notes. The above equation can be inverted to provide

$$\epsilon_{ij} = \frac{1}{2\mu}\left(\sigma_{ij} - \frac{\lambda}{3\lambda + 2\mu}\delta_{ij}\sum_{i=1}^{i=3}\sigma_{ij}\right) \tag{2}$$

The elastic energy part of the total energy is given by,

$$U = \sum_{i,j}\frac{1}{2}\sigma_{ij}\epsilon_{ij} \tag{3}$$

Consider a simple case of cylinder under tensile stress in Z direction. For this case, only one component of stress tensor is nonzero: $\sigma_{11} = T$, $\sigma_{22} = 0$, $\sigma_{33} = 0$ and $\sigma_{12} = \sigma_{23} = \sigma_{13} = 0$.

From Eq. 2 ,

$$\epsilon_{11} = \frac{1}{2\mu}\sigma_{11} - \frac{\lambda}{3\lambda + 2\mu}\sigma_{11} \tag{4}$$

$$= ET \tag{5}$$

where E is the Youngs modulus of the material.

The elastic energy for this deformation is given by

$$U = \sigma_{11} * \epsilon_{11} \tag{6}$$

$$= T\epsilon_{11} \tag{7}$$

In the above equation for energy, the sign of energy depends only on ϵ_{11} component (T is given positive quantity).

$$\epsilon_{11} = ET \tag{8}$$

$$= \frac{\lambda(1 + \nu)(1 - 2\nu)}{\nu}.T \tag{9}$$

From the above equation, it is clear that the sign of $\epsilon_1 1$ (consequently, the elastic energy) is positive only for values of $\nu < \frac{1}{2}$.

Solution 8.2

The Gibbs-Duhem expression for two phases in equilibrium with fixed compo-

sition is given by,

$$-S^\alpha dT^\alpha + V^\alpha dP^\alpha - \sum_i N_i^\alpha d\mu_i \quad = \quad 0 \tag{10}$$

$$-S^\beta dT^\beta + V^\beta dP^\beta - \sum_i N_i^\beta d\mu_i \quad = \quad 0 \tag{11}$$

For equilibrium between the phases, at the coexistence curve, the chemical potential, consequently change in chemical potential, of any species in these phases need to be equal, *i.e.*, $d\mu_i^\alpha = d\mu_i^\beta = d\mu$. Similarly $dP^\alpha = dP^\beta = dP$ and $dT^\alpha = dT^\beta = dT$.

$$-S^\alpha dT + V^\alpha dP - \sum_i N_i^\alpha d\mu = 0 \tag{12}$$

$$-S^\beta dT + V^\alpha dP - \sum_i N_i^\beta d\mu = 0 \tag{13}$$

For a single component system, the compositions are fixed, leading to relations

$$-\bar{S}^\alpha dT + \bar{V}^\alpha dP - d\mu = 0 \tag{14}$$
$$-\bar{S}^\beta dT + \bar{V}^\beta dP - d\mu = 0 \tag{15}$$

Subtracting the above relation from the previous one, and rearranging

$$\frac{dP}{dT} = \frac{\bar{S}^\alpha - \bar{S}^\beta}{\bar{V}^\alpha - \bar{V}^\beta} \tag{16}$$

$$= \frac{\bar{\Delta S}}{\bar{\Delta S}} \tag{17}$$

Physically Clausius Clapeyron equation provides a relation between thermodynamic potentials for the phases at equilibrium.

Solution 8.3

At the tri-critical point all three phases are at equilibrium. The equilibrium conditions on thermodynamic potentials are $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \mu_i$, $T^\alpha = T^\beta = T^\gamma$ and $P^\alpha = P^\beta = P^\gamma$. It is also given that $X_A^\alpha = 1 - X_B^\alpha$, $X_A^\alpha = 1 - X_B^\alpha$ and $X_A^\gamma = 1 - X_B^\gamma$.

The Clausius-Clapeyron equation for the system at equilibrium,

$$-\bar{S}^\alpha dT^\alpha + \bar{V}^\alpha dP^\alpha - X_A^\alpha d\mu_A^\alpha - X_B^\alpha d\mu_B^\alpha \quad = \quad 0 \tag{18}$$
$$-\bar{S}^\beta dT^\beta + \bar{V}^\beta dP^\beta - X_A^\beta d\mu_A^\beta - X_B^\beta d\mu_B^\beta \quad = \quad 0 \tag{19}$$
$$-\bar{S}^\gamma dT^\gamma + \bar{V}^\gamma dP^\gamma - X_A^\gamma d\mu_A^\gamma - X_B^\gamma d\mu_B^\gamma \quad = \quad 0 \tag{20}$$

Applying the conditions on thermodynamic potentials and rearranging the terms,

$$-\bar{S}^\alpha dT + \bar{V}^\alpha dP - X_A^\alpha(d\mu_A - d\mu_B) \quad = \quad d\mu_B \tag{21}$$
$$-\bar{S}^\beta dT + \bar{V}^\beta dP - X_A^\beta(d\mu_A - d\mu_B) \quad = \quad d\mu_B \tag{22}$$
$$-\bar{S}^\gamma dT + \bar{V}^\gamma dP - X_A^\gamma(d\mu_A - d\mu_B) \quad = \quad d\mu_B \tag{23}$$

Since RHS of the above equations are same, they can be compared with each other. Equating Eqs. 21 and 23 with Eq. 22 gives,

$$d\mu_A - d\mu_B = \frac{-(S^\beta - S^\gamma)dT + (V^\beta - V^\gamma)dP}{(X_A^\beta - X_A^\gamma)} \tag{24}$$

$$d\mu_A - d\mu_B = \frac{-(S^\alpha - S^\beta)dT + (V^\alpha - V^\beta)dP}{(X_A^\alpha - X_A^\beta)} \tag{25}$$

On simplification the above two equations give,

$$dP = \left(\frac{\Delta V^{\beta \to \gamma}}{\Delta X^{\beta \to \gamma}} - \frac{\Delta V^{\alpha \to \beta}}{\Delta X^{\alpha \to \beta}}\right)^{-1} \left(\frac{\Delta S^{\beta \to \gamma}}{\Delta X^{\beta \to \gamma}} - \frac{\Delta S^{\alpha \to \beta}}{\Delta X^{\alpha \to \beta}}\right) dT \tag{26}$$

where $\Delta(.)^{\alpha \to \beta} = (.)^\alpha - (.)^\beta$. Also, $\Delta S^{\alpha \to \beta}$ can be written in terms of the enthalpy of transformation and the equilibrium transformation temperature.

To find the relation between $d\mu_A$ and $d\mu_B$ substitute Eq. 26 into Eq. 21 and Eq. 22 then eliminate dT. On simplifying, the following equation gives the relation between the changes in chemical potential of the two species at the triple point.

$$\frac{d\mu_A}{d\mu_B} = \frac{\bar{S}^\gamma(\bar{V}^\beta - \bar{V}^\beta X_A^\alpha + \bar{V}^\alpha(-1 + X_A^\beta)) + \bar{S}^\alpha(\bar{V}^\gamma - \bar{V}^\gamma X_A^\beta + \bar{V}^\beta(-1 + X_A^\gamma)) + \bar{S}^\beta(\bar{V}^\alpha + \bar{V}^\gamma(-1 + X_A^\alpha) - \bar{V}^\alpha X_A^\gamma)}{(-\bar{S}^\gamma \bar{V}^\beta X_A^\alpha + \bar{S}^\beta \bar{V}^\gamma X_A^\alpha + \bar{S}^\gamma \bar{V}^\alpha X_A^\beta - \bar{S}^\alpha \bar{V}^\gamma X_A^\beta - \bar{S}^\beta \bar{V}^\alpha X_A^\gamma + \bar{S}^\alpha \bar{V}^\beta X_A^\gamma)} \tag{27}$$

Solution 8.4

The *engineering* solution for problem 2 in PS5 is

$$T_f = \frac{1}{L_i \alpha - \beta}[L_i \alpha T_i - \beta T_0] \tag{28}$$

where,

$$\alpha = \frac{1}{L_0}\frac{dL}{dT} \tag{29}$$

is the coefficient of linear thermal expansion of the material, $\beta = 0.005 m/K$, T_0 is the initial temperature of the Infinite Corridor, and T_i and T_f are the initial and final temperatures of the *diabolic* thermostat.

Let us assume the initial conditions as given in the problem statement : the temperature of the Infinite Corridor $T_0 = 20C$, and the thermostat also points to the same temperature, the whole system of infinite corridor and thermostat is in equilibrium. The stability of the equilibrium is determined by applying small disturbance to this equilibrium state and examining the magnitude of growth or decay of disturbance.

Let us apply a small perturbation or disturbance ΔT to the initial temperature T_0 $(T_0 \to T_0 + \Delta T)$.

The final temperature would be governed by the equation for T_f

$$T_f + \Delta T' = \frac{1}{L_i \alpha - \beta}[L_i \alpha T_i - \beta(T_0 + \Delta T)] \tag{30}$$

or the change in final temperature is given by,

$$\Delta T' = \frac{\beta}{\beta - L_i \alpha}\Delta T \tag{31}$$

Written in a more transparent way,

$$\frac{\Delta T'}{\Delta T} = \frac{\beta}{\beta - L_i \alpha} \tag{32}$$

In the above equation ΔT is the applied disturbance and $\Delta T'$ is the resulting change. So the condition for stability is given by

$$\left| \frac{\Delta T'}{\Delta T} \right| \leq 1.0 \tag{33}$$

which implies, for stability the following inequality must be obeyed.

$$\left| \frac{\beta}{\beta - L_i \alpha} \right| \leq 1.0, \tag{34}$$

where $| * |$ is absolute magnitude of $*$.