14.15: Problems

Problems

1. When we express the energy of a system as a function of entropy, volume, and composition, we have $E=E\left(S,V,n_1,n_2,\dots,\ n_\omega\right)$. Since S and V are extensive variables, we have $\lambda E=E\left(\lambda S,\lambda V,\lambda n_1,\lambda n_2,\dots,\ \lambda n_\omega\right)$. Find $\left(\partial\left(\lambda E\right)/\partial\lambda\right)_{SV}$. From this result, show that

$$G=\sum^{\omega}_{j=1}\mu_jn_j$$

2. When we express the energy of a system as a function of pressure, temperature, and composition, we have $E=E\left(P,T,n_1,n_2,\dots,\ n_\omega\right)$. Because P and T are independent of λ, $\lambda E=E\left(P,T,\lambda n_1,\lambda n_2,\dots,\ \lambda n_\omega\right)$. Show that

$$E=\sum^{\omega}_{j=1}\overline{E}_jn_j$$

3. From $E=\mathrm{E}\left(P,T,n_1,n_2,\dots,\ n_\omega\right)$ and the result in problem 2, show that

$$\left[\left(\frac{\partial H}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P\right]dT+\left[P\left(\frac{\partial V}{\partial P}\right)_T+T\left(\frac{\partial V}{\partial T}\right)_P\right]dP=\sum^{\omega}_{j=1}n_jd\overline{E}_j$$

Note that at constant pressure and temperature,

$$\sum^{\omega}_{j=1}n_jd\overline{E}_j=0$$

4. If pressure and temperature are constant, $E=E\left(n_1,n_2,\dots,\ n_\omega\right)$ and $\lambda E=E\left(\lambda n_1,\lambda n_2,\dots,\ \lambda n_\omega\right)$. Show that $\sum^{\omega}_{j=1}n_jd\overline{E}_j=0$ follows from these relationships.

5. A solution contains n_1 moles of component 1, n_2 moles of component 2, n_3 moles of component 3, *etc*. Let $n=n_1+n_2+n_3+\dots$ The mole fraction of component j is $x_j=n_j/n$. Show that

$$\left(\frac{\partial x_j}{\partial n_j}\right)=\frac{n-n_j}{n^2}$$

and, for $j\neq k$,

$$\left(\frac{\partial x_j}{\partial n_k}\right)=\frac{-n_j}{n^2}$$

What are

$$\left(\frac{\partial x_1}{\partial n_1}\right)$$

and

$$\left(\frac{\partial x_2}{\partial n_2}\right)$$

if the solution has only two components?

6. For any extensive state function, $Y\left(P,T,n_1,n_2,\dots,\ n_\omega\right)$, the arguments developed in this chapter lead, at constant P and T, to the equations

$$Y=n_1\overline{Y}_1+n_2\overline{Y}_2+\dots+n_\omega\overline{Y}_\omega$$

and

$$0=n_1d\overline{Y}_1+n_2d\overline{Y}_2+\dots+n_\omega d\overline{Y}_\omega$$

Where $\overline{Y}_j$ is the partial molar quantity $(\partial Y/\partial n_j)_{P,T,n_{m\neq j}}$.

(a) Prove that $0 = x_1 d\overline{Y}_1 + x_2 d\overline{Y}_2 + \cdots + x_\omega d\overline{Y}_\omega$

(b) Prove that

$$0 = n_1 \left(\frac{\partial \overline{Y}_1}{\partial n_1}\right) + n_2 \left(\frac{\partial \overline{Y}_2}{\partial n_2}\right) + \cdots + n_\omega \left(\frac{\partial \overline{Y}_\omega}{\partial n_\omega}\right)$$

(c) Prove that

$$0 = x_1 \left(\frac{\partial \overline{Y}_1}{\partial x_1}\right) + x_2 \left(\frac{\partial \overline{Y}_2}{\partial x_2}\right) + \cdots + x_\omega \left(\frac{\partial \overline{Y}_\omega}{\partial x_\omega}\right)$$

7. The enthalpy of mixing is measured in a series of experiments in which solid solute, A, dissolves to form an aqueous solution. These enthalpy data are represented well by empirical equations $\Delta_{mix} H = \alpha_1 \underline{m} + \alpha_2 \underline{m}^2$, $\alpha_1 = \beta_{11} + \beta_{12} (T - 273.15)$ and $\alpha_2 = \beta_{21} + \beta_{22} (T - 273.15)$ with

$$\beta_{11} = 10.0 \text{ kJ molal}^{-1}$$

$$\beta_{12} = -0.14 \text{ kJ molal}^{-2}\ K^{-1}$$

$$\beta_{21} = -3.00 \text{ kJ molal}^{-1}$$

$$\beta_{22} = -0.040 \text{ kJ molal}^{-2}\ K^{-1}$$

Find $\overline{L}_A$, $\overline{L}_{H_2O}$, $\overline{J}_A$, and $\overline{J}_{H_2O}$ as functions of $\underline{m}_A$ and T. Find $\overline{L}_A$, $\overline{L}_{H_2O}$, $\overline{J}_A$, and $\overline{J}_{H_2O}$ for a one molal solution at 209 K. What is the value of

$$\ln \frac{\tilde{a}_A (1 \text{ molal}, 290 \text{ K})}{\tilde{a}_A (1 \text{ molal}, 273.15 \text{ K})}$$

Notes

[1] We can make other assumptions. It is possible to describe an inhomogeneous system as a collection of many macroscopic, approximately homogeneous regions.