

Solutions to Homework Problem Set 12

Stowe 11.40

(a) In this problem, we are supposed to find dS as a function of independent variables dT and dP . We may write $dS = \frac{\partial S}{\partial T}|_P dT + \frac{\partial S}{\partial P}|_T dP$. $\frac{\partial S}{\partial T}|_P = \frac{1}{T} \frac{T \partial S}{\partial T}|_P = \frac{C_P}{T}$. Using Maxwell relations, $\frac{\partial S}{\partial P}|_T = -\frac{\partial V}{\partial T}|_P = -V\beta$. Therefore, $dS = \frac{C_P}{T} dT - V\beta dP$.

(b) By integrating the above equation over T and P independently, we get $\Delta S = \int dS = \int \frac{C_P}{T} dT - \int V\beta dP = C_P \ln(T_f/T_i) - V\beta(P_f - P_i)$. With the numbers given, for mole of water, we get

$$\Delta S = 75.3 \text{ J/K/mol} \ln \frac{373 \text{ K}}{273 \text{ K}} - 1.8 \times 10^{-5} \text{ m}^3/\text{mole} \times 2.1 \times 10^{-4} \text{ /K} \times 10000 \times 1.013 \times 10^5 \text{ Pa} = 19.7 \text{ J/K}$$

Reif 5.12

The system is thermally insulated and evolves quasi-statically, so the constraint can be written as $dS = 0$. In this problem, we may write dS as a function of dT and dP and then use the constraint to find the relationship between dT and dP . There is $dS = \frac{\partial S}{\partial T}|_P dT + \frac{\partial S}{\partial P}|_T dP = \frac{C_P}{T} dT - V\beta dP$ (see the first problem). Since $dS = 0$, there is $\frac{C_P}{T} dT - V\beta dP = 0$, so $dT = \frac{TV\beta}{C_P} dP = \frac{T\beta}{c_p \rho} dP$. Here $c_p = C_P/m$, and $\rho = m/V$. When the changes in temperature and pressure are very small, we do not integrate the above differentials but may directly write $\delta T = \frac{T\beta}{c_p \rho} \Delta P$.

Reif 5.15

(a) In this case, the work done by the surface tension force is $dW = -\sigma da$ where σ is the surface tension force and $da = 2l dx$ is the change in area. There is a $-$ sign because the direction of the tension force is always opposite to the direction of dx , i.e., when the film is stretched, the tension force points in the direction opposite to the stretch. Therefore, the first law for this system is $dE = dQ - dW = dQ + 2l\sigma dx$. Note that in comparison with the first law for the gas $dE = dQ - PdV$, $-2l\sigma$ is equivalent to P and x is equivalent to V in the thermodynamic relations.

(b) We may use the second law to re-write the first law as $dE = TdS + 2l\sigma dx$, and first find dS as a function of T and the external variable x . We may write $dS = \frac{\partial S}{\partial T}|_x dT + \frac{\partial S}{\partial x}|_T dx$. Under the constant temperature, dT term is zero. And using the Maxwell relations for the generalized force and displacement, we get $\frac{\partial S}{\partial x}|_T = \frac{\partial(-2l\sigma)}{\partial T}|_x = 2l\alpha$. Now using the first law, we get $dE = TdS + 2l\sigma dx = 2lT\alpha dx + 2l\sigma dx = 2l\sigma_0 dx$. Therefore, $\Delta E = E(x) - E(0) = \int_0^x 2l\sigma_0 dx = 2l\sigma_0 x$.

(c) From (a), the work done by the surface tension force is $W = \int dW = -2l\sigma dx = -2lx\sigma$.