

Solutions to Homework Problem Set 11

Stowe 10.3

(a) From $S = CV^2 \ln E$, we can find right away $\frac{1}{T} = \frac{\partial S}{\partial E}|_V = \frac{CV^2}{E}$.

(b) $\frac{P}{T} = \frac{\partial S}{\partial V}|_E = 2CV \ln E$.

(c) From (a), there is $E = CV^2 T$, so $\frac{\partial E}{\partial V}|_T = 2CTV$.

(d) From (d), there is $P = 2CV T \ln E = \frac{2E \ln E}{V} = \frac{2S}{CV^3} e^{\frac{S}{CV^2}}$, so $\frac{\partial P}{\partial V}|_S = -\frac{2S}{CV^4} e^{\frac{S}{CV^2}} (3 + \frac{2S}{CV^2})$.

Stowe 10.42

By definition, $C_P = \partial Q / \partial T|_P$. Now we use the second law to write the expression of dQ as $dQ = dE + PdV$ and then express dE as the function of independent variables T and V as $dE = \frac{\partial E}{\partial T}|_V dT + \frac{\partial E}{\partial V}|_T dV$. The first term is just C_V , and the second term is $\frac{\partial E}{\partial V}|_T = T \frac{\partial P}{\partial T}|_V - P$ (see class notes). So the second law becomes $dQ = C_V dT + T \frac{\partial P}{\partial T}|_V dV$, and therefore, $\frac{\partial dQ}{\partial T}|_P = C_V + T \frac{\partial P}{\partial T}|_V \frac{\partial V}{\partial T}|_P$, or $C_P - C_V = T \frac{\partial P}{\partial T}|_V \frac{\partial V}{\partial T}|_P$.

For the real gas, we will use the Van Der Waals equation $(P + \frac{a}{v^2})(v - b) = RT$ to find the partial derivatives above. By differentiating the Van der Waals equation and organizing terms, we arrive at $(v - b)dP + (P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3})dv = RdT$. Therefore, $\frac{\partial P}{\partial T}|_V = \frac{R}{v-b} = 3.08 \times 10^4 \text{ J/K/m}^3$, and $\frac{\partial V}{\partial T}|_P = \frac{R}{P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}} = 1.61 \times 10^{-6} \text{ m}^3/\text{K/mol}$. Also, using the Van der Waals equation, we can calculate the temperature as $T = (P + \frac{a}{v^2})(v - b)/R = 529 \text{ K}$. So $C_P - C_V = T \frac{\partial P}{\partial T}|_V \frac{\partial V}{\partial T}|_P = 26.2 \text{ J/K/mol}$.

Note: if you use the equation given in Stowe's book, the right equation for the real gas is $C_P - C_V = \frac{R}{B}(1 + \frac{a}{v^3})$, where $B = (1 - \frac{a}{pv^2} + 2abpv^3)$.

Stowe 10.45

(a) Differentiate this equation by parts, keeping in mind that P , V , and T are all variables, there is $2PT^{-1/3}e^{aV}dP - \frac{1}{3}T^{-4/3}P^2e^{aV}dT + aP^2T^{-1/3}e^{aV}dV = 0$, or $2dP - \frac{1}{3T}PdT + aPdV = 0$. So $dV = \frac{1}{3aT}dT - \frac{2}{aP}dP$.

(b) Let $dT = 0$, we get $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}|_T = \frac{2}{aPV}$.

(c) Let $dP = 0$, we get $\beta = \frac{1}{V} \frac{\partial V}{\partial T}|_P = \frac{1}{3aTV}$.