

Solutions to Homework Problem Set 15

Stowe 13.7

(a) The gas starts with P_1 and V_1 . At the end of the first stage of isochorical heating, the state is P_2 and $V_2 = V_1$.

For the second stage of adiabatic expansion, there is the adiabatic relation for an ideal gas $P_2V_2^\gamma = P_3V_3^\gamma$, so at the end of the second stage, $P_3 = P_2(\frac{V_2}{V_3})^\gamma = P_2(\frac{V_1}{V_3})^\gamma$.

At the end of the third stage of isochorical cooling, $V_4 = V_3$. Assuming that the pressure is P_4 , then for the last stage of adiabatic compression, there is the adiabatic relation $P_4V_4^\gamma = P_1V_1^\gamma$, resulting in $P_4 = P_1(\frac{V_1}{V_4})^\gamma = P_1(\frac{V_1}{V_3})^\gamma$.

Eventually at the end of the last stage, the system returns to the initial state of P_1 and V_1 .

(b) In the first stage, $dV = 0$, so $W = \int PdV = 0$. From the first law, $Q = \Delta E = nc_V\Delta T = nc_V(T_2 - T_1) = \frac{c_V}{R}(P_2V_2 - P_1V_1) = \frac{c_V}{R}(P_2 - P_1)V_1$.

In the second stage, $Q = 0$, $W = \int_2^3 PdV = (P_2V_2 - P_3V_3)/(\gamma - 1)$ (see solution to Reif2.10 in HW set 4). From the expression of V_2 and P_3 above, we get $W = P_2V_1[1 - (\frac{V_1}{V_3})^{\gamma-1}]/(\gamma - 1)$.

In the third stage, since $dV = 0$, $W = 0$. $Q = \Delta E = nc_V\Delta T = nc_V(T_4 - T_3) = \frac{c_V}{R}(P_4V_4 - P_3V_3) = \frac{c_V}{R}(P_4 - P_3)V_3$. Using the expressions of P_4 and P_3 from (a), we get $Q = \frac{c_V}{R}(P_1 - P_2)(\frac{V_1}{V_3})^\gamma V_3$.

In the last stage, $Q = 0$, $W = \int_4^1 PdV = \frac{P_4V_4 - P_1V_1}{\gamma - 1} = P_1V_1[(\frac{V_1}{V_3})^{\gamma-1} - 1]/(\gamma - 1)$.

Stowe 13.7 for the Van der Waals gas

For the Van der Waals gas, we will use the equation of the state $(P - \frac{a}{v^2})(v - b) = RT$ and discuss the situation for 1 mole gas.

(a) At the end of the first stage of isochorical heating, the state of the gas is P_2 and $V_2 = V_1$.

For the second stage of adiabatic expansion, we use the adiabatic relation for the Van der Waals gas $T_2(v_2 - b)^{R/c_V} = T_3(v_3 - b)^{R/c_V}$ to find $T_3 = T_2[(v_2 - b)/(v_3 - b)]^{R/c_V}$. From the Van der Waals equation, we get $T_2 = (P_2 - \frac{a}{v_2^2})(v_2 - b)/R = (P_2 - \frac{a}{v_1^2})(v_1 - b)/R$, so $T_3 = (P_2 - \frac{a}{v_1^2})(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V}/R$, and $P_3 = RT_3/(v_3 - b) - \frac{a}{v_3^2} = (P_2 - \frac{a}{v_1^2})[(v_1 - b)/(v_3 - b)]^{R/c_V+1} - \frac{a}{v_3^2}$.

At the end of the third stage, $v_4 = v_3$, and the pressure P_4 can be derived by using the adiabatic relation in the last stage. The adiabatic relation is such $T_4(v_4 - b)^{R/c_V} = T_1(v_1 - b)^{R/c_V}$, resulting in $T_4 = T_1[(v_1 - b)/(v_4 - b)]^{R/c_V} = T_1[(v_1 - b)/(v_3 - b)]^{R/c_V}$. From the Van der Waals equation, $T_1 = (P_1 - \frac{a}{v_1^2})(v_1 - b)/R$, so $T_4 = (P_1 - \frac{a}{v_1^2})(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V}/R$. And $P_4 = RT_4/(v_4 - b) - \frac{a}{v_4^2} = (P_1 - \frac{a}{v_1^2})(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V+1} - \frac{a}{v_3^2}$.

Eventually at the end of the last stage, the system returns to the initial state of P_1 and v_1 .

(b) To derive heat and work, we make use of the expression of the internal energy of the Van der

Waals gas $E = c_V T - \frac{a}{v} + \text{const.}$

In the first stage, since $dv = 0$, $W = 0$, so $Q = \Delta E = c_v(T_2 - T_1) - a(1/v_2 - 1/v_1) = c_v(T_2 - T_1)$. From the expressions of T_2 and T_1 in (a), we get $Q = \frac{c_V}{R}[(P_2 - \frac{a}{v_2^2})(v_2 - b) - (P_1 - \frac{a}{v_1^2})(v_1 - b)] = \frac{c_V}{R}(P_2 - P_1)(v_1 - b)$.

In the second stage, $Q = 0$, $W = -\Delta E = c_V(T_2 - T_3) - a(1/v_2 - 1/v_3)$. Using the expressions of T_2 and T_3 in (a), we get $W = \frac{c_V}{R}[(P_2 - \frac{a}{v_2^2})(v_2 - b) - (P_2 - \frac{a}{v_1^2})(v_1 - b)][(v_2 - b)/(v_3 - b)]^{R/c_V} - a(1/v_2 - 1/v_3) = \frac{c_V}{R}[(P_2 - \frac{a}{v_1^2})(v_1 - b) - (P_2 - \frac{a}{v_1^2})(v_1 - b)][(v_1 - b)/(v_3 - b)]^{R/c_V} - a(1/v_1 - 1/v_3) = \frac{c_V}{R}(P_2 - \frac{a}{v_1^2})(v_1 - b)(1 - [(v_1 - b)/(v_3 - b)]^{R/c_V}) - a(1/v_1 - 1/v_3)$.

In the third stage, $W = 0$, and $Q = \Delta E = c_v(T_4 - T_3) = \frac{c_V}{R}[(P_1 - \frac{a}{v_1^2})(v_1 - b)][(v_1 - b)/(v_3 - b)]^{R/c_V} - (P_2 - \frac{a}{v_1^2})(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V} = \frac{c_V}{R}(P_1 - P_2)(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V}$.

In the last stage, $Q = 0$, and $W = -\Delta E = c_V(T_4 - T_1) - a(1/v_4 - 1/v_1) = \frac{c_V}{R}[(P_1 - \frac{a}{v_1^2})(v_1 - b)][(v_1 - b)/(v_3 - b)]^{R/c_V} - (P_1 - \frac{a}{v_1^2})(v_1 - b) - a(1/v_3 - 1/v_1) = \frac{c_V}{R}(P_1 - \frac{a}{v_1^2})(v_1 - b)[(v_1 - b)/(v_3 - b)]^{R/c_V} - 1) - a(1/v_3 - 1/v_1)$.

Compare heat and work for the Van der Waals gas with those for the ideal gas, it is seen that P for the real gas is replaced by $P - \frac{a}{v^2}$, and V is replaced by $v - b$. In addition, in the non-isochorical stages, the change in the internal energy of the Van der Waals gas should also include the change in the interaction potential energy a/v .

Importantly, for the Van der Waals gas, $c_P \neq c_V + R$, so $\gamma - 1 \neq R/c_V$. Therefore, we cannot directly use γ in the expressions of heat and work for the Van der Waals gas. We may find the ratio of specific heats for the Van der Waals gas in the following approach: $dQ = TdS = T\partial S/\partial T|_V dT + T\partial S/\partial V|_T dV$. Using the Maxwell relation $\partial S/\partial V|_T = \partial P/\partial T|_V$ and the definition $c_V = T\partial S/\partial T|_V$, the above becomes $dQ = T\partial S/\partial T|_V dT + T\partial P/\partial T|_V dV = c_V dT + T\partial P/\partial T|_V dV$. By definition, $c_P = \partial Q/\partial T|_P = c_V + T\partial P/\partial T|_V \partial V/\partial T|_P$. The partial derivatives on the righthand side of the equation may be derived by differentiating the Van der Waals equation: $(v - b)dP + [P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}]dV = RdT$, which gives $\partial P/\partial T|_v = R/(v - b)$ and $\partial v/\partial T|_P = R/[P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3}]$. Therefore, $c_P = c_V + R^2 T/[(v - b)[P + a/v^2 - 2a(v - b)/v^3]] = c_V + R^2 T/[RT - 2a(v - b)^2/v^3]$, and $\gamma = c_P/c_V = 1 + R/c_V RT/[RT - 2a(v - b)^2/v^3]$.