[tex202] Heat capacities of the Dieterici gas

The thermodynamic equation of state for 1mol of a Dieterici gas reads

$$p = \frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right).$$

For a full thermodynamic specification of this system, a caloric equation of state needs to be established from empirical information, e.g. in the form of a heat capacity C_V or C_p. However, C_V cannot be freely invented. It must be compatible with the thermodynamic equation of state. One such condition follows from the fact that the differential of $U(T,V)$ is exact:

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right]_V \;\Rightarrow\; \left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial T}\left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\}\right]_V.$$

Another such condition can be derived from the thermodynamic equation of state as follows:

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

(a) Determine $(\partial C_V/\partial V)_T$ from the Dieterici gas from the thermodynamic equation of state and show that it vanishes in the ideal gas limit.
(b) Determine $C_p - C_V$ from the Dieterici thermodynamic equation of state and confirm the consistency in the limit $a, b \to 0$ with the known ideal gas result, $C_p - C_V = R$.

Solution: