HEAT CAPACITIES IN TERMS OF ENTROPY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 3.33.

The thermodynamic identity for an infinitesimal process is

$$dU = TdS - PdV \tag{1}$$

For constant volume processes $dV = 0$, so we can derive the expression for the heat capacity by dividing both sides by dT:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{2}$$

For constant pressure processes, the heat capacity is defined in terms of the enthalpy. The enthalpy is defined as

$$H = U + PV \tag{3}$$

It is the energy required to create the system, which is a combination of the internal energy U of the system itself, plus the work required to clear the volume V that the system occupies. If this work is done at constant pressure, the work is PV. In a system in which the only work done is from expansion, $H = Q$ so the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{4}$$

The change in H is

$$\begin{aligned} dH &= dU + PdV + VdP & (5)\\ &= TdS - PdV + PdV + VdP & (6)\\ &= TdS + VdP & (7) \end{aligned}$$

At constant pressure $dP = 0$ so dividing both sides by dT we get

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{8}$$

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