

HEAT CAPACITIES IN TERMS OF ENTROPY

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The thermodynamic identity for an infinitesimal process is

$$dU = TdS - PdV \quad (1)$$

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

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

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

$$H = U + PV \quad (3)$$

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

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

The change in H is

$$dH = dU + PdV + VdP \quad (5)$$

$$= TdS - PdV + PdV + VdP \quad (6)$$

$$= TdS + VdP \quad (7)$$

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

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