

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

$$(0.1) \quad dU = TdS - PdV$$

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

$$(0.2) \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

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

$$(0.3) \quad H = U + PV$$

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

$$(0.4) \quad C_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$$

The change in H is

$$(0.5) \quad dH = dU + PdV + VdP$$

$$(0.6) \quad = TdS - PdV + PdV + VdP$$

$$(0.7) \quad = TdS + VdP$$

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

$$(0.8) \quad C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

PINGBACKS

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