Heat capacities in enthalpy and entropy calculations

Enthalpy calculations

Consider adding a fixed amount of heat Q to a closed system initially at temperature T_1, at constant pressure. We would like to know the final temperature T_2. Applying the first law, we find that:

$$dU^t = \delta Q + \delta W$$
$$= \delta Q - P dV^t$$

We can rearrange this equation:

$$\delta Q = n dU + n P dV$$

Substituting $U = H - PV$:

$$\delta Q = n[dH - P dV - V dP] + n P dV$$
$$= n dH - n V dP$$

Since the pressure is constant, $dP = 0$ and this expression simplifies so we can integrate:

$$\delta Q = n dH$$

$$Q = n \Delta H$$

By definition, $C_P \equiv \left(\frac{dH}{dT}\right)_P$, and so we can write:

$$Q = n \int_{T_1}^{T_2} C_P \, dT$$

If the heat capacity is constant, we find that $Q = n C_P (T_2 - T_1)$. On the other hand, in general the heat capacity can be temperature-dependent. A general temperature-dependent *empirical* form for the heat capacity for ideal gases and incompressible liquids is:

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$$

where $A, B, C,$ and D are substance-dependent constants and T is absolute temperature. Substituting this into the enthalpy integral and performing the integration, we arrive at:

$$Q = nR \left[A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3) - D(T_2^{-1} - T_1^{-1}) \right]$$

At this point, we could plug in the known values of everything and solve for T_2, but we would need a fairly robust nonlinear equation solver, since there are several terms involving T_2. A better approach would be to iterate, where we can provide a controlled initial guess.

To set up the equation for iteration, we put it in the same form as the case for constant heat capacity. To do this, we multiply and divide by $(T_2 - T_1)$:

$$Q = n \frac{R\left[A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3) - D(T_2^{-1} - T_1^{-1})\right]}{(T_2 - T_1)} (T_2 - T_1)$$

$$= n \langle C_P \rangle_H (T_2 - T_1)$$

where we have defined the average heat capacity $\langle C_P \rangle_H$ using the expression:

$$\langle C_P \rangle_H \equiv \frac{R\left[A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3) - D(T_2^{-1} - T_1^{-1})\right]}{(T_2 - T_1)}$$

Here the subscript "H" indicates that the average heat capacity is computed with respect to enthalpy calculations. Note that $\langle C_P \rangle_H$ is also dependent on T_2, the temperature for which we are solving. Thus, we need to perform an iteration. Rearranging our main equation,

$$T_2 = T_1 + \frac{Q}{n \langle C_P \rangle_H}$$

To solve for T_2, we provide an initial guess, compute $\langle C_P \rangle_H$, and then compute a new value for T_2 using the equation above. We continue this process until T_2 converges.

For numerical reasons, it is often more convenient to express the average heat capacity using T_1 and the ratio of the temperatures $\tau \equiv T_2/T_1$, rather than T_2. Making the substitution $T_2 = \tau T_1$ in the above equation, $\langle C_P \rangle_H$ can also be written as:

$$\langle C_P \rangle_H = R\left[A + \frac{B}{2}T_1(\tau + 1) + \frac{C}{3}T_1^2(\tau^2 + \tau + 1) + DT_1^{-1}\tau^{-1}\right]$$

Entropy calculations

Let's say we want to compute the entropy change in the same case as above, where the temperature of the system changes from the same T_1 to T_2 at constant pressure. Since entropy is a state function, it doesn't matter what process we conceptualize for this change, and we will pick a reversible process as the most convenient. Starting again with the first law, simplified from the previous example:

$$\delta Q = n \mathrm{d}H$$

Substituting in $\delta Q_{rev} = nTdS$:

$$dS = \frac{dH}{T}$$

$$= \frac{C_P dT}{T}$$

where we have used the definition of C_P as before. Integrating,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

If the heat capacity is constant, we arrive at:

$$\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right)$$

On the other hand, if the heat capacity follows the same substance-dependent form as before, we can again substitute and integrate to get:

$$\Delta S = R\left[A \ln\left(\frac{T_2}{T_1}\right) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) - \frac{D}{2}(T_2^{-2} - T_1^{-2})\right]$$

We would like to put this expression in the same form as the constant heat capacity case:

$$\Delta S = \frac{R\left[A \ln(T_2/T_1) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) - \frac{D}{2}(T_2^{-2} - T_1^{-2})\right]}{\ln\left(\frac{T_2}{T_1}\right)} \ln\left(\frac{T_2}{T_1}\right)$$

$$= \langle C_P \rangle_S \ln\left(\frac{T_2}{T_1}\right)$$

Where we have defined a different average heat capacity $\langle C_P \rangle_S$ to be:

$$\langle C_P \rangle_S \equiv \frac{R\left[A \ln(T_2/T_1) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) - \frac{D}{2}(T_2^{-2} - T_1^{-2})\right]}{\ln\left(\frac{T_2}{T_1}\right)}$$

$$= R\left\{A + \left[B\,T_1 + \left(C\,T_0^2 + \frac{D}{\tau^2 T_0^2}\right)\left(\frac{\tau + 1}{2}\right)\right]\left(\frac{\tau - 1}{\ln \tau}\right)\right\}$$

with $\tau \equiv T_2/T_1$ as before. Note that the average heat capacity used in entropy calculations is different from that used for enthalpy calculations, as indicated by the subscripts "S" and "H", respectively.

Also note that, if T_2 is not specified and ΔS is given, we would have to solve iteratively for T_2 using the rearranged expression:

$$T_2 = T_1 \exp\left(\frac{\Delta S}{\langle C_P \rangle_S}\right)$$