

## General Expression for the internal energy U and the enthalpy H

$$dU = C_v \cdot dT + \left[ T \cdot \left( \frac{d}{dT} P \right) - P \right] \cdot dV$$

$$dH = C_p \cdot dT + \left[ V - T \cdot \left( \frac{d}{dT} V \right) \right] \cdot dP$$

Special cases: 1) ideal gases  
2) constant volume and pressure processes

1 ideal gases: the second term on both expression is zero

$$dU = C_v \cdot dT$$

$$dH = C_p \cdot dT$$

2. Constant volume the second term in dU equals zero and at constant pressure the second term in dH equals zero

$$dU = C_v \cdot dT$$

$$dH = C_p \cdot dT$$

To calculate the enthalpy from the heat capacity at constant pressure  $C_p$  you need to integrate the expression of  $C_p$  in the range of temperatures.

$$\Delta H = \int_{T_1}^{T_2} C_p(T) dT$$

Finally for real gases the internal energy U has two terms; the first term is  $U_0$  (standard internal energy) and the second term is called the imperfection internal energy  $U_i$ .

This latter term is given by

$$U_i = \int_{\infty}^V \left[ T \cdot \left( \frac{\delta P}{\delta T} \right) - P \right] dV$$

If you use the Redlich-Kwong expression for P in the following form and use Symbolics and the differentiate you will get

$$P(V, T) = \frac{R \cdot T}{V - b} - \frac{a}{\sqrt{T} \cdot V \cdot (V - b)}$$

$$\frac{d}{dT}P(V, T) = \frac{R}{V - b} + \frac{1}{2} \cdot \frac{a}{T^{\frac{3}{2}} \cdot V \cdot (V - b)}$$

then  $U_i$  is given by

$$U_i = \int_{\infty}^V \left[ T \cdot \left[ \frac{R}{V - b} + \frac{1}{2} \cdot \frac{a}{T^{\frac{3}{2}} \cdot V \cdot (V - b)} \right] - P \right] dV$$

and the final equation for  $U_i$  is

$$U_i(V, T) = \frac{3}{2} \cdot \frac{a}{\sqrt{T} \cdot b} \cdot \ln \left( \frac{V}{V + b} \right)$$