

## Abstract

Consider a system with a homogeneous fluid of constant composition. Suppose we are tasked with calculating the enthalpy and entropy of the system using simple pressure, temperature, and volume data obtained from running operations at various conditions. We wish to derive simple formulas for enthalpy and entropy using Maxwell's equations [1].

## Derivation

$$H = F(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (1)$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \text{ [definition of constant pressure heat capacity]} \quad (2)$$

$$\text{Substituting (2) into (1), we have: } dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (3)$$

$$H = U + PV \text{ [definition of enthalpy]}$$

$$\text{Differentiating, } dH = dU + PdV + VdP \quad (4)$$

$$U = W + Q \text{ [definition of internal energy]}$$

$$dU = dW + dQ \quad (5)$$

$$\text{Substituting (5) into (4), we have } dH = dW + dQ + PdV + VdP \quad (6)$$

$$dW = -PdV, dS = dQ/T \text{ [definitions of work and entropy]}$$

$$dH = -PdV + TdS + PdV + VdP$$

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

$$\text{Dividing by } dP \text{ keeping temperature constant, } \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad (8)$$

$$\text{Plugging (8) into (3), we have: } dH = C_p dT + \left(V + T\left(\frac{\partial S}{\partial P}\right)_T\right) dP \quad (9)$$

From Maxwell's equations, we know that:  $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$  (10)

$$\text{Thus, } dH = C_p dT + [V - T\left(\frac{\partial V}{\partial T}\right)_P] dP$$

$$S = F(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (11)$$

Taking the partial derivative of (7) with respect to temperature at constant pressure, we have:

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\text{Using (2), } C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\text{Thus, } dS = C_p \frac{dT}{T} + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (12)$$

$$\text{Substituting (10) into (12), we find: } dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

## Discussion

These results allow us to calculate enthalpy and entropy with a few parameters: first, the constant pressure heat capacity ( $C_p$ ) must be known; this constant is species specific and sometimes

tabulated. Second,  $\left(\frac{\partial V}{\partial T}\right)_P$  is needed for the calculations, and it can be found as it is the relation of

volume change as temperature changes at constant pressure. To do this, the system can be run at

constant pressure with controllable, varying temperature. Volume should be measured at various

temperatures and the data can be modeled using an appropriate regression method to yield an

approximation for  $\left(\frac{\partial V}{\partial T}\right)_P$  to use in the calculation.

It is worth noting that  $C_p$  is not always well defined or is only valid for a range of low pressures and the second term would be a model of data, however these values still serve as solid estimates to find constructed thermodynamic variables (enthalpy, entropy) of a system for real application.

## References

1. "The Maxwell Relations." *LibreTexts Chemistry*. *LibreTexts*,  
[chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/  
Physical\\_Chemistry\\_\(LibreTexts\)/22%3AHelmholtz\\_and\\_Gibbs\\_Energies/22.03%3A\\_  
The\\_Maxwell\\_Relations](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(LibreTexts)/22%3AHelmholtz_and_Gibbs_Energies/22.03%3A_The_Maxwell_Relations).