An example and explanation of the
DeHoff Method in Thermodynamics

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The DeHoff method is a way to obtain an expression for any thermodynamic parameter, in terms of any other two parameters. This allows us to construct useful expressions in terms of easily measurable quantities (temperature and pressure), as well as expressions that link seemingly unrelated parameters like entropy, Helmholtz energy, and volume. This method relies on the bank of equations below. These equations can be derived from the definitions of each parameter, and a bit of tricky algebra.

DeHoff Equations:

$dV = V\alpha_V dT - V\beta_T dP$

$dS = \frac{C_p}{T} dT - V\alpha_V dP$

$dU = (C_P - PV\alpha_V)dT - V(T\alpha_V - P\beta_T)dP$

$dH = C_P dTV(1 - T_V)dP$

$dF = -(S - PV\alpha_V)dT + PV\beta_T dP$

$dG = VdP - SdT$

Example

Find Gibbs energy as a function of entropy and volume
$(G = f(S, V))$
First we take the total differential of for G. This is also referred to as the 'chain rule' in calculus.

$$dG = \left(\frac{\partial G}{\partial V}\right)_S dV + \left(\frac{\partial G}{\partial S}\right)_V dS \tag{1}$$

To simplify the rest of the computation, we make the following substitutions for the partial derivatives.

$$M = \left(\frac{\partial G}{\partial V}\right)_S \tag{2}$$

$$N = \left(\frac{\partial G}{\partial S}\right)_V \tag{3}$$

$$dG = MdV + NdS \tag{4}$$

Now Substitute in from known relations for temperature and pressure only, taken from the table above.

$$dV = V\alpha_V dT - V\beta_T dP \tag{5}$$

$$dS = \frac{C_p}{T}dT - V\alpha_V dP \tag{6}$$

$$dG = M\left(V\alpha_V dT - V\beta_T dP\right) + N\left(\frac{C_p}{T}dT - V\alpha_V dP\right) \tag{7}$$

Group dT terms and dV terms together.

$$dG = MV\alpha_V dT - MV\beta_T dP + \frac{NC_p}{T}dT - NV\alpha_V dP \tag{8}$$

$$dG = MV\alpha_V dT + \frac{NC_p}{T}dT - MV\beta_T dP - NV\alpha_V dP \tag{9}$$

$$dG = \left(MV\alpha_V + \frac{NC_p}{T}\right)dT + \left(-MV\beta_T - NV\alpha_V\right)dP \tag{10}$$

Now we compare this to the known formula for G as a function of T and P, again referencing the table above.

$$dG = -SdT + VdP \tag{11}$$

The coefficients of the dT term in this expression, must be equal to the coefficients for the dT term in the derived expression. Likewise for dP. As such, we can set them equal.

$$-S = MV\alpha_V + \frac{NC_p}{T} \tag{12}$$

$$V = -MV\beta_T - NV\alpha_V \tag{13}$$

We can start by simplifying the second expression.

$$V = -MV\beta_t - NV\alpha_v = V(-M\beta t - N\alpha_v) \tag{14}$$

$$1 = -M\beta t - N\alpha_v \tag{15}$$

$$M = \frac{1 + N\alpha_v}{-\beta_t} \tag{16}$$

Now we can substitute this expression in for M in the other derived expression.

$$-S = \left(\frac{1 + N\alpha_v}{-\beta_t}\right) V\alpha_v + \frac{NC_p}{T} \tag{17}$$

Now we attempt to solve for N.

$$-S = \frac{V\alpha_v + N\alpha_v^2 V}{-\beta_t} + \frac{NC_p}{T} \tag{18}$$

$$S\beta_t T = TV\alpha_v + TN\alpha_v^2 V - \beta_t NC_p \tag{19}$$

$$S\beta_t T - TV\alpha_v = TN\alpha_v^2 V - \beta_t NC_p \tag{20}$$

$$S\beta_t T - TV\alpha_v = N\left(T\alpha_v^2 V - \beta_t C_p\right) \tag{21}$$

$$\frac{S\beta_t T - TV\alpha_v}{T\alpha_v^2 V - \beta_t C_p} = N \tag{22}$$

Now we can substitute this expression for N into our derived definition of M.

$$M = \frac{1 + \left(\frac{S\beta_t T - TV\alpha_v}{T\alpha_v^2 V - \beta_t C_p}\right)\alpha_v}{-\beta_t} \tag{23}$$

This can be simplified significantly.

$$M = \frac{C_P - T\alpha_v S}{TV\alpha_v^2 - C_P\beta_t} \tag{24}$$

Now we can reconstruct the entire expression for G in terms of S and V.

$$dG = MdV + NdS \tag{25}$$

$$dG = \left(\frac{C_P - T\alpha_v S}{TV\alpha_v^2 - C_P\beta_t}\right) dV + \left(\frac{S\beta_t T - TV\alpha_v}{T\alpha_v^2 V - \beta_t C_p}\right) dS \tag{26}$$

Now we can attempt to check the units on this expression, one term at a time, first the dV term.

$$\left(\frac{[E/T] - [T][1/T][E/T]}{[T][V][1/T^2] - [E/T][1/P]}\right) dV \tag{27}$$

$$\left(\frac{[E/T] - [E/T]}{[V/T] - [E/T][1/P]}\right) dV \tag{28}$$

$$[E/P] = [V] \tag{29}$$

$$\left(\frac{[E/T] - [E/T]}{[V/T] - [V/T]}\right) dV \tag{30}$$

$$[E/V]dV = [E] \tag{31}$$

$$\left(\frac{[E/T][1/P][T] - [T][V][1/T]}{[T][1/T^2][V] - [1/P][E/T]}\right) dS \tag{32}$$

$$\left(\frac{[E/P] - [V]}{[V/T] - [1/P][E/T]}\right) dS \tag{33}$$

$$\left(\frac{[V] - [V]}{[V/T] - [V/T]}\right) dS \tag{34}$$

$$[T]dS = [T][E/T] = [E] \tag{35}$$

Both terms yield energy, the correct units for Gibbs energy.