# Thermodynamics Quick Summary

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Use of Thermodynamic Squares

The thermodynamic square is a mnemonic device to recall thermodynamic potentials and their conjugate variables. A common version uses the phrase *"Great Physicists Have Studied Under Very Fine Teachers"* to represent the potentials G, F, H, and U (which happens on the sides of the square) with their respective variables T, S, P, and V (at the corners). Each side of the square pairs conjugate variables.
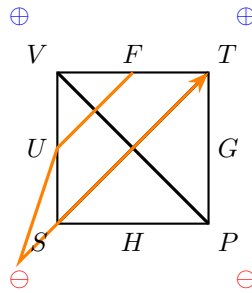
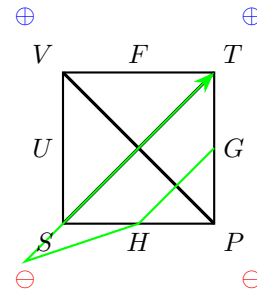Here is a depiction of the thermodynamic square:
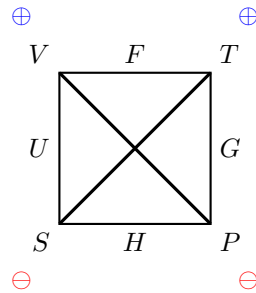
The thermodynamic potentials and their relations can be obtained from the thermodynamics square, i.e., from the square, imagine start at any potential, then go to any other potential adjacent to it, then follow along the diagonal to multiply the variables at the corner, taking the sign at the corner with it:
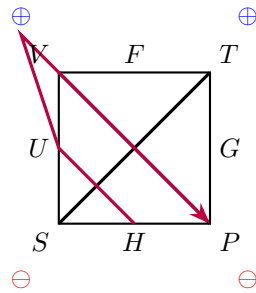
$$H = U + PV \qquad\qquad F = U - TS \qquad\qquad G = H - TS$$

Thus, we can obtain the following relations:

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$$H = U + PV \quad \text{(enthalpy)} \tag{1}$$

$$F = U - TS \quad \text{(Helmholtz free energy)} \tag{2}$$

$$G = H - TS \quad \text{(Gibbs free energy)} \tag{3}$$

$$U = F + TS \quad \text{(internal energy)} \tag{4}$$

These can be traversed clockwise or counterclockwise around the square.

We can use the squares to obtain the fundamental equations of thermodynamics or the thermodynamic differentials. Choose a potential, then we are going to take the variables (and the signs) opposite the potential and each variable multiplied by the differential of the variable along its diagonal, and add them, as shown below:

$$dH = V\,dp + T\,dS \qquad\qquad dU = T\,dS - P\,dV \qquad\qquad dF = -P\,dV - S\,dT$$
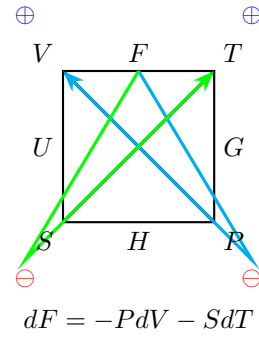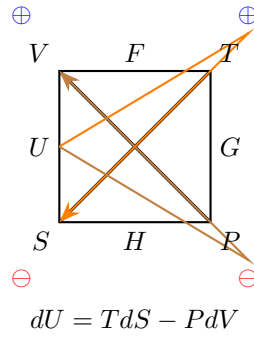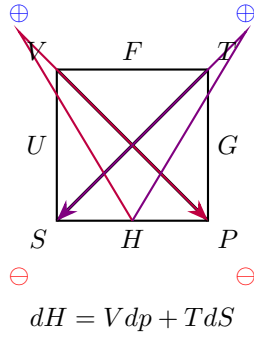
Note: As one uses these relations more and more frequently, it is perhaps easier to recall these relations from memory without drawing and setting up the square in the first instance.

Maxwell Relations

From the fundamental equations above, we can derive Maxwell relations.

Relating Change of S to Change of V

Suppose we want to relate the change of S to the change of V. We will use these variables that are *not* differentials, so that a second partial derivative of them can be taken, i.e., we use:

$$dG = -S\,dT + V\,dP \tag{5}$$

Eq. (5) implies that G is a function of both T and P (seen from dT and dP). We can obtain the complete differential of Eq. (5):

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \tag{6}$$

Equating the terms, we get:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \tag{7}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V. \tag{8}$$

Taking the mixed derivatives (with respect to both T and P) of G:

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial P}(-S) = -\left(\frac{\partial S}{\partial P}\right)_T, \text{ substituting (7).} \tag{9}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial T}(V) = \left(\frac{\partial V}{\partial T}\right)_P, \text{ substituting (8).} \tag{10}$$

Since dG is an exact differential, we have:

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \tag{11}$$

Equating these (Eq. (9) and (10)) using the exact differential condition, we obtain:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P. \tag{12}$$

Relating S and P

If instead, we need to relate S and P, we use:

$$dF = -S\,dT - P\,dV \tag{13}$$

Then, we have:

$$\left(\frac{\partial(-S)}{\partial V}\right)_T = \left(\frac{\partial(-P)}{\partial T}\right)_V \tag{14}$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{15}$$

Proof: Change in Internal Energy for Isothermal Expansion of a Perfect Gas

Now, let's prove that the change in internal energy for an isothermal expansion of a perfect/ideal gas is zero, i.e.,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for perfect gases} \tag{16}$$

We start from:

$$dU = T\,dS - P\,dV \tag{17}$$

Since we want $\left(\frac{\partial U}{\partial V}\right)_T$, we need $U = U(V, T)$. Therefore, we replace dS in Eq. (17).

We write $S = S(V, T)$, then:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{18}$$

Substitute Eq. (18) into Eq. (17):

$$dU = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV - P \, dV \tag{19}$$

$$= T \left(\frac{\partial S}{\partial T} \right)_V dT + \left[T \left(\frac{\partial S}{\partial V} \right)_T - P \right] dV \tag{20}$$

Comparing to partial derivatives of U

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \tag{21}$$

and equating terms, we have

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P \tag{22}$$

Now, replace $\left(\frac{\partial S}{\partial V} \right)_T$ using Maxwell relation. Using thermodynamic differential containing conjugate variables V and T:

$$dF = -S \, dT - P \, dV \tag{23}$$

$$\implies \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \tag{24}$$

and substituting Eq. (24) into Eq. (22)

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \tag{25}$$

For a perfect gas, the equation of state is:

$$P = \frac{nRT}{V} \tag{26}$$

Thus:

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \tag{27}$$

Substitute Eq. (27) into Eq. (25)

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{nR}{V} \right) - P = P - P = 0 \tag{28}$$

Q.E.D.