Summary of Mathematical Tricks in Thermodynamics

Most of these tricks involve going from unfamiliar thermodynamic derivatives to more familiar ones. You will need these especially when you are not dealing with ideal gases.

1) Writing state functions in terms of their natural variables - Full differentials

$$U = U(S,V,N)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$dU = TdS - pdV + \mu dN$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N},\ p = -\left(\frac{\partial U}{\partial V}\right)_{S,N},\ \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

2) Writing state functions in terms of other state variables

$$U = U(S,V,N)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V} dT + \left(\frac{\partial U}{\partial V}\right)_{T} dV$$

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_{T} dV$$

3) Legendre Transforms - switching natural variables

$$A(T,V,N) = U(S,V,N) - TS$$

$$dA = dU - d(TS)$$

$$dA = (TdS - pdV + \mu dN) - TdS - SdT$$

$$dA = -SdT - pdV + \mu dN$$

4) Maxwell Relations - Obtain partial derivative relations from a full differential

$$dU = TdS - pdV + \mu dN$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N}$$

$$-\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N}$$

5) Triple Product Rule (Cyclic Rule) - Relation between partial derivatives

$$\left(\frac{\partial S}{\partial V}\right)_{T}\left(\frac{\partial V}{\partial T}\right)_{S}\left(\frac{\partial T}{\partial S}\right)_{V} = -1$$

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6) Change of Variables - Replace one exact differential with an expanded form, changes variable being held constant

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

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

Replace dp using $dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV$ to obtain

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV\right]$$

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V\right] dT + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T dV$$

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V\right] dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Compare to the first expression to find that

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

Some of the questions on Problem Set 2 will require these relations. For example, in your derivation of adiabatic work, you will need to show that

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

Showing this requires the use of natural variable expansion and a Maxwell relation. Can you obtain this result on your own?