

STEM for VA:

# Chemical Thermodynamics

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**Abstract:** Thermodynamics plays a key role

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# 1 Introduction

Chemical thermodynamics revolves around internal energy (U), Gibbs energy (G), Helmholtz energy (A), enthalpy (H). The language we use to describe these things is multi-variate calculus, but we don't need anything terribly complicated. The partial derivative follows all the same rules as a derivative save for one, and the differential is an easy pattern to understand.

## 1.1 Differentials

When considering a multi-variable function  $f = f(x_1, x_2, \dots, x_n)$ , a differential is an infinitesimal change in that multi-variable function. The general form for the **total differential** of a multi-variable function of  $n$  variables is as follows:

$$df(x_1, x_2, \dots, x_n) = \left( \frac{\partial f}{\partial x_1} \right)_{i \neq j} dx_1 + \left( \frac{\partial f}{\partial x_2} \right)_{i \neq j} dx_2 + \dots + \left( \frac{\partial f}{\partial x_n} \right)_{i \neq j} dx_n \quad (1.1)$$

where  $x_i$  is used to reference the variables  $f$  is a function of. We see the general pattern is the partial derivative of the function with respect to one of its variables multiplied by the differential of the same variable. The subscript  $i \neq j$  means that the partial derivative only cares about the variable indexed by  $i$  and is constant in all other variables. As an example:

$$f(x, y) = 6yx^2 \implies df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy = (12yx) dx + (6x^2) dy$$

Here, we leverage the nice feature of partial derivatives where we treat everything other than the variable in question as a constant. As such,

$$\left( \frac{\partial f}{\partial x} \right)_y = \left( \frac{\partial}{\partial x} \right)_y [6yx^2] = 12yx \implies \left( \frac{\partial f}{\partial y} \right)_x = \left( \frac{\partial}{\partial y} \right)_x [6yx^2] = 6x^2$$

It's important to note that the chain rule and product rule among others would still apply if relevant. We denote what  $f$  is constant with respect to when taking these partial derivatives by placing subscripts after the parenthesis. This choice is very important and should not be forgotten when writing out your partial derivatives. Lastly, the order of application for partial derivatives don't matter when differentiating something is an *exact differential*.  $\frac{\partial^2}{\partial x \partial y} = \frac{\partial^2}{\partial y \partial x}$ .

## 1.2 Energies

With 1.1 established, let's first write out the four relevant total differentials:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad (1.2)$$

$$dH = \left( \frac{\partial H}{\partial S} \right)_P dS + \left( \frac{\partial H}{\partial P} \right)_S dP \quad (1.3)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP \quad (1.4)$$

$$dA = \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV \quad (1.5)$$

Here, the portions in bold denote what each energy is a function of based on how total differentials are defined (i.e. referring to 1.1). We can see that

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

$$H = H(S, P)$$

$$G = G(T, P)$$

$$A = A(T, V)$$

Now, the hopeful question one might ask is how we found these energies to be functions of their particular *natural* variables. The answer is we start with internal energy (U) and perform what's called a *Legendre Transform*. This sounds scarier than it is, so I'll elaborate.

The first thing to note is that the concept of *conjugate variables* exist. You see temperature and entropy paired together, so they are conjugate. The same holds true with volume and pressure — moles and chemical potential. They are variables where, when considering their units, produce units of energy upon multiplication. Let's take temperature and entropy:  $T \text{ [K]} \times S \text{ [J/K]} = U \text{ [J]}$ .

Simply put, the Legendre transform involves subtracting conjugate variables from a state function. Let's consider Helmholtz energy. It is *defined* as

$$A = U - TS. \quad (1.6)$$

The reason this produce 1.5 is because if we differentiate, we get:

$$dA = dU - TdS - SdT$$

Of course, we know  $dU = TdS - PdV$ , so we're left with

$$dA = TdS - PdV - TdS - SdT.$$

$$dA = -SdT - PdV \quad (1.7)$$

Pattern matching, we see that the differentials are now  $dT$  and  $dV$  meaning  $A$  is a function of volume and temperature. We can follow the same procedure for Gibbs energy and enthalpy.

$$H = U + PV \quad (1.8)$$

$$dH = dU + PdV + VdP$$

$$dH = TdS + VdP \quad (1.9)$$

Notice here that we add  $PV$  rather than subtract. The reason is that we've defined the  $PV$  work with a negative sign, so addition is what will undo it, procedurally speaking.

$$G = U + PV - TS \quad (1.10)$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = -SdT + VdP \quad (1.11)$$

Gibbs energy requires both adding  $PV$  and subtracting  $TS$  since it's the "opposite" of internal energy when considering their natural variables.  $V \rightarrow P$  and  $S \rightarrow T$  when comparing the two.

It's important to note that you can express the thermodynamic quantities in terms of their "unnatural" variables as well. Take

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV. \quad (1.12)$$

From this, you can re-write

$$dU = TdS - PdV \implies dU = \underbrace{\left[ T \left( \frac{\partial S}{\partial T} \right)_V \right]}_{\left( \frac{\partial U}{\partial T} \right)_V} dT + \underbrace{\left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right]}_{\left( \frac{\partial U}{\partial V} \right)_T} dV$$

**Note.** The second term  $[x]dV$  should differ from what it normally is since we're now keeping  $T$  rather than  $S$  constant. The important thing to note here is that the coefficients for the differentials,  $dT$  and  $dV$ , are now very complicated signaling  $U$  is **not** a natural variable of one or both of the two. Of course, we know temperature is the problem here.

### 1.3 Thermodynamic Definitions

With the machinery of Section 1.1 and 1.2 established, we can write out thermodynamic definitions for these partial derivatives. Let's start off with U again.

$$dU = \underbrace{TdS}_{\delta q} - \underbrace{PdV}_{\delta w}$$

If we compare this equation to Eqn. 1.2, we see that the only differences are the appearance of T and -P which replace the partial derivatives. The reason being is that scientists *defined* thermodynamic values to be equivalent to these partial derivatives. Writing them out formally:

$$dU : \left( \frac{\partial U}{\partial S} \right)_V = +T \rightarrow \left( \frac{\partial U}{\partial V} \right)_S = -P \quad (1.13)$$

$$dH : \left( \frac{\partial H}{\partial S} \right)_P = +T \rightarrow \left( \frac{\partial H}{\partial P} \right)_S = +V \quad (1.14)$$

$$dG : \left( \frac{\partial G}{\partial T} \right)_P = -S \rightarrow \left( \frac{\partial G}{\partial P} \right)_T = +V \quad (1.15)$$

$$dA : \left( \frac{\partial A}{\partial T} \right)_V = -S \rightarrow \left( \frac{\partial A}{\partial V} \right)_T = -P \quad (1.16)$$

Once again, the denominator of the partial derivative is bolded to emphasize the natural variables of the functions.

### 1.4 Maxwell Relations

Maxwell relations leverage the fact that, for state functions (or exact differentials, whatever you'd like to call them), the *cross-derivatives* are equal. That is to say if  $f = f(x, y)$ :

$$df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy$$

If we arbitrarily label  $a = \left( \frac{\partial f}{\partial x} \right)_y$  and  $b = \left( \frac{\partial f}{\partial y} \right)_x$ , we can re-write the above expression as

$$df = adx + bdy$$

which shouldn't be unfamiliar since this re-writing is the crux of Section 1.3. (a, b become T, V, P, etc.). Now, if we take our cross-derivative, we can show that

$$\left( \frac{\partial a}{\partial y} \right)_x = \left( \frac{\partial b}{\partial x} \right)_y$$

which is really equal to

$$\left( \frac{\partial^2 f}{\partial y \partial x} \right) = \left( \frac{\partial^2 f}{\partial x \partial y} \right)$$

Recall that derivatives are applied left to right (more generally, *operators* act on things that lie to their right like  $\hat{H}\Psi$ ) so we see that the left term with  $\partial y \partial x$  in the denominator means that  $\partial x$  was applied first **then**  $\partial y$ . The opposite is true for the right side;  $\partial y$  **then**  $\partial x$ .

With this established, let's look back at Eqn. 1.9-1.12 to see how we can apply this concept.

$$dU = TdS - PdV \begin{cases} T \equiv \left( \frac{\partial U}{\partial S} \right)_V \\ -P \equiv \left( \frac{\partial U}{\partial V} \right)_S \end{cases}$$

so we can write

$$\left( \frac{\partial T}{\partial V} \right)_S = \left( \frac{\partial (-P)}{\partial S} \right)_V \rightarrow \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

If we want to "formally" write these expressions, it works out to be

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V \right]_S = \left[ \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S \right]_V$$

$$\underbrace{\left(\frac{\partial^2 U}{\partial V \partial S}\right)}_{\left(\frac{\partial T}{\partial V}\right)_S} = \underbrace{\left(\frac{\partial^2 U}{\partial S \partial V}\right)}_{-\left(\frac{\partial P}{\partial S}\right)_V}$$

Writing out all the Maxwell relations:

$$dU : \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (1.17)$$

$$dH : \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (1.18)$$

$$dG : -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (1.19)$$

$$dA : -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \quad (1.20)$$

So that you can look in one spot and get the majority of the information:

Table 1: Summary of Concepts

Fundamental Eqn.	Implication	Maxwell Relation	Natural Var.
$dU = TdS - PdV$	$\left(\frac{\partial U}{\partial S}\right)_V = T \rightarrow \left(\frac{\partial U}{\partial V}\right)_S = -P$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	U(S, V)
$dH = TdS + VdP$	$\left(\frac{\partial H}{\partial S}\right)_P = T \rightarrow \left(\frac{\partial H}{\partial P}\right)_S = V$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	H(S, P)
$dG = -SdT + VdP$	$\left(\frac{\partial G}{\partial T}\right)_P = -S \rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V$	$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$	G(T, P)
$dA = -SdT - PdV$	$\left(\frac{\partial A}{\partial T}\right)_V = -S \rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -P$	$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$	A(T, V)

## 2 Examples

For this stuff, it's important to recall the product rule (or quotient if you want to do more work). Suppose we have  $U/T$  and we wanted to find  $\frac{\partial}{\partial T}[U/T]_V$ . How would we do it? Well, we have to use the product rule! Recall

$$\frac{d}{dx}[f(x)g(x)] = g(x) \cdot \frac{df}{dx} + f(x) \cdot \frac{dg}{dx}$$

The other thing to remember, at least in the case of our toy problem above, is that

$$\frac{d}{dx}[x^n] = nx^{n-1}$$

If  $n$  happens to be a negative number, the pattern still works. Equipped with this, let's tackle the problem.

### 2.1 Example 1

$$\frac{\partial}{\partial T}[U/T]_V = \frac{\partial}{\partial T}\left[U \cdot \frac{1}{T}\right]_V = \frac{\partial}{\partial T}[U \cdot T^{-1}]_V$$

Applying the product rule and exponent rule:

$$\frac{\partial}{\partial T}[U/T]_V = \left\{\frac{1}{T} \cdot \left(\frac{\partial U}{\partial T}\right)_V\right\} + \left\{\left(-\frac{1}{T^2}\right)U\right\}$$

If we remember  $C_V \equiv (\partial U/\partial T)_V$ , we can slightly simplify the above expression to

$$\frac{\partial}{\partial T}\left[\frac{U}{T}\right]_V = \frac{C_V}{T} - \frac{U}{T^2}$$

## 2.2 Example 2

Suppose we want to relate the temperature dependence of the Gibbs free energy to the system enthalpy. We know  $G = H - TS$  (which is why  $\Delta G = \Delta H - T\Delta S$  at constant temperature), so let's start here. If we divide  $T$  over, we get

$$\frac{G}{T} = \frac{H}{T} - S$$

We will, somewhat arbitrarily, decide to partially differentiate this expression with respect to  $T$  while keeping pressure fixed since Gibbs is a function of temperature and pressure.

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \underbrace{-\frac{H}{T^2} + \frac{1}{T} \cdot \left(\frac{\partial H}{\partial T}\right)_P}_{\text{Prod. Rule}} - \left(\frac{\partial S}{\partial T}\right)_P$$

By definition,  $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$  and  $\frac{C_P}{T} \equiv \left(\frac{\partial S}{\partial T}\right)_P$  so the two terms cancel out leaving you with the Gibbs-Helmholtz equation.

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2} \quad (2.1)$$

Similar relationships can be found with the other thermodynamic quantities.

## 2.3 Example 3

This is likely something you wouldn't have to know, but it could be good to see. We will derive the total differential for entropy here.

$$dU = TdS - PdV \implies TdS = dU + PdV$$

By definition,  $C_V dT = dU$  so we'll make that substitution here.

$$TdS = C_V dT + PdV$$

Divide over temperature.

$$dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

Writing out some definitions again that we won't prove:

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V \quad \text{and} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_T$$

thus

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