

# Derivative Crusher Algorithm

by Ratindranath Akhoury

EVAN CARPENTER

Winter 2022

**Idea:** A partial derivative with thermodynamically significant variables  $\left(\frac{\partial x}{\partial y}\right)_z$  where  $\{x, y, z\}$  can be any of  $\{S, T, P, V, E, F, G, H\}$  can be expressed in terms of first and second derivatives of fundamental relations. This re-arranging of expressions is very useful in thermodynamics and statistical mechanics, as it allows us to find simple relations between physical quantities in a thermodynamical system. The Derivative Crusher Algorithm is an algorithm that "crushes" a thermodynamically significant partial derivative into useful and easily measureable quantities. Developed and taught by Professor Ratindranath Akhoury.

## 1 Background

Variable	Easy to keep fixed?	Easy to measure change?
$S$	<b>Yes</b> , Adiabatic processes	<b>No</b> , change in $S$ depends on change in $Q$ , which is hard to measure
$T$	<b>Yes</b> , with a heat bath or feedback system	<b>Yes</b> , by using a thermometer
$V$	<b>No</b> , not easily, thermal expansion of the container is a byproduct of the container being thermally conductive, the volume changes with heat	<b>Yes</b>
$P$	<b>Yes</b> , keeping equilibrium with atmosphere	<b>Yes</b> , barometer

Table 1:  $T, P$  are the easiest quantities to measure and control, making  $G(T, P)$  the easiest fundamental relationship to work with.

Looking at  $G(T, P) = E - TS - PV$  more closely:

$$\begin{aligned} \left(\frac{\partial G}{\partial T}\right)_P &= -S & \left(\frac{\partial G}{\partial P}\right)_T &= V \\ \left(\frac{\partial^2 G}{\partial T^2}\right)_P &= -\left(\frac{\partial S}{\partial T}\right)_P \equiv \frac{C_p}{T} & \left(\frac{\partial^2 G}{\partial P^2}\right)_T &= \left(\frac{\partial V}{\partial P}\right)_T \equiv \kappa V \\ \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right] &= \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \alpha V \end{aligned}$$

$C_p$  is specific heat at constant pressure.

$\kappa$  is isothermal compressibility.

$\alpha$  is volume coefficient of expansion.

## 1.1 Background

The derivative crusher algorithm is made of three partial derivative operations:

1. Bringing  $y$  to the numerator:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

2. Bringing  $z$  to the numerator:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}$$

3. Introduce new variable  $w$ :

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial w}\right)_z}{\left(\frac{\partial y}{\partial w}\right)_z}$$

## 2 Steps

1. Bring potentials  $E, F, G, H$  to the numerator and eliminate them using:

$$dE = TdS - PdV$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$dH = TdS + VdP$$

2. Bring  $S$  to numerator using Maxwell Relations depending on what  $z$  is in  $\left(\frac{\partial x}{\partial y}\right)_z$

$$z = T \quad \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

$$z = P, V \quad \boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}}$$

3. Bring  $V$  to numerator in order to get  $\alpha$  or  $\kappa$ .
4. Eliminate  $C_v$  in favor of  $C_p, \alpha, \kappa$