

Thermodynamic Calculus manipulations :

(18b)

① inversion / reciprocal rule : $\left(\frac{\partial x}{\partial y}\right)_z = 1 / \left(\frac{\partial y}{\partial x}\right)_z$

Same as single variable result

Since z is fixed here.

example : $\left(\frac{\partial V}{\partial T}\right)_P = 1 / \left(\frac{\partial T}{\partial V}\right)_P$

② triple product rule / cyclic relation

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

example / proof : consider $P(T, V)$.

We have $dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$

Now hold P constant so that $dP = 0$.

Then we can combine the differentials dT and dV at constant P conditions :

$$0 = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial P}{\partial V}\right)_T$$

rearranging and using

the inversion rule gives the triple product rule.

③ addition of variable / chain rule

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

example : $\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial P}\right)_V \left(\frac{\partial P}{\partial T}\right)_V$

④ non-natural derivative / chain rule

(18c)

$$A(x, y) \rightarrow \left. \frac{\partial A}{\partial y} \right|_z = \left. \frac{\partial A}{\partial y} \right|_x + \left. \frac{\partial A}{\partial x} \right|_y \left. \frac{\partial x}{\partial y} \right|_z$$

example / proof :

$$H = H(T, P) \Rightarrow dH = \left. \frac{\partial H}{\partial T} \right|_P dT + \left. \frac{\partial H}{\partial P} \right|_T dP$$

Now divide by dT at constant V :

$$\left. \frac{\partial H}{\partial T} \right|_V = \left. \frac{\partial H}{\partial T} \right|_P \cdot 1 + \left. \frac{\partial H}{\partial P} \right|_T \left. \frac{\partial P}{\partial T} \right|_V$$

This is a special case of the more general chain rule :
Consider F in terms of either (x, y) or (u, v)

$$\text{Then } \left. \frac{\partial F}{\partial x} \right|_y = \left. \frac{\partial F}{\partial u} \right|_v \left. \frac{\partial u}{\partial x} \right|_y + \left. \frac{\partial F}{\partial v} \right|_u \left. \frac{\partial v}{\partial x} \right|_y$$

⑤ Exact and inexact differentials

An expression $M(x, y)dx + N(x, y)dy$ is exact if there exists an f such that $M = \left. \frac{\partial f}{\partial x} \right|_y$ and $N = \left. \frac{\partial f}{\partial y} \right|_x$

How to test : use the fact that $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ for any

analytic function f .

Therefore, exact iff $\left. \frac{\partial M}{\partial y} \right|_x = \left. \frac{\partial N}{\partial x} \right|_y$