Partial Differentiation

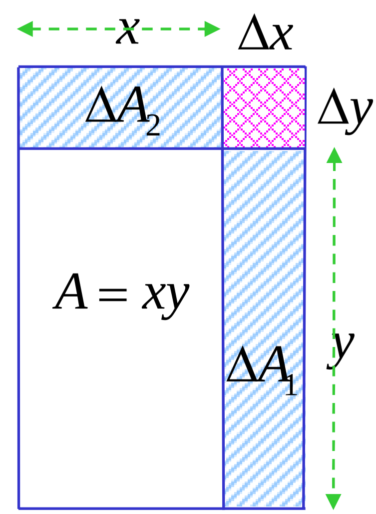
for functions of more than one variable: $f = f(x, y, \ldots)$

Take area as an example $A = xy$

For an increase Δx in x, $\Delta A_1 = y\Delta x$ y constant

For an increase Δy in y, $\Delta A_2 = x\Delta y$ x constant

For a simultaneous increase



$$\Delta A = (x + \Delta x)(y + \Delta y) - xy$$
$$= y\Delta x + x\Delta y + \Delta x\Delta y$$
$$= \frac{\Delta A_1}{\Delta x}\Delta x + \frac{\Delta A_2}{\Delta y}\Delta y + \Delta x\Delta y$$

In the limits $\Delta x \to 0, \quad \Delta y \to 0$

$$\Delta A \to dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy$$

total differential

partial differential

for a real single-value function *f* of two independent variables,

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{\delta x \to 0}\left\{\frac{f(x + \delta x, y) - f(x, y)}{\delta x}\right\}$$

Partial Derivative Relations

Consider $f(x,y,z)=0$, so $z=z(x,y)$

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

- Partial derivatives can be taken in any order.

$$\frac{\partial^2 z}{\partial x\partial y}=\frac{\partial^2 z}{\partial y\partial x} \qquad \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y=\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x$$

- Taking the inverse: $\left[\left(\frac{\partial z}{\partial x}\right)_y\right]^{-1}=\left(\frac{\partial x}{\partial z}\right)_y$

- To find the third partial derivative:

$$dz=0 \quad \Rightarrow \quad \left(\frac{\partial z}{\partial y}\right)_x dy=-\left(\frac{\partial z}{\partial x}\right)_y dx$$

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

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

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

Partial Derivatives in Thermodynamics

From the generalized equation of state for a closed system,

$$f\left(P,V,T\right)=0$$

six partial derivatives can be written:

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

but given the three inverses, e.g $\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^{-1}=\left(\frac{\partial T}{\partial V}\right)_P$

and the chain rule $\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T=-1$

there are only two *independent* "basic properties of matter". By convention these are chosen to be:

the coefficient of thermal expansion (isobaric), and $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

the coefficient of isothermal compressibility. $\kappa=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

The third derivative is simply

$$\left(\frac{\partial P}{\partial T}\right)_V=-\frac{\left(\partial V/\partial T\right)_P}{\left(\partial V/\partial P\right)_T}=\frac{\alpha}{\kappa}$$

The Euler Relation

Suppose $\delta z = A(x,y)\,dx + B(x,y)\,dy$

Is δz an exact differential, i.e. *dz*?

dz is exact provided $\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$ cross-differentiation

because then

$$A = \left(\frac{\partial z}{\partial x}\right)_y \qquad \left(\frac{\partial A}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

$$B = \left(\frac{\partial z}{\partial y}\right)_x \qquad \left(\frac{\partial B}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

The corollary also holds.

State functions have exact differentials.

Path functions do not.

New thermodynamic relations may be derived from the Euler relation.

e.g. given that $dU = TdS - PdV$

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