$\text{if } dS > 0$; $\text{if } \mu_1^{I} > \mu_1^{II}$

$(T^{I} = T^{II} = T)$

$$dS = \left(\frac{\mu_1^{II}}{T^{II}} - \frac{\mu_1^{I}}{T^{I}} \right) dN_1^{I} = \left(\frac{\mu_1^{II} - \mu_1^{I}}{T} \right) dN_1^{I}$$

$T^{II}, T^{I} \to T$

*

$\Rightarrow dN_1^{I} < 0 \Rightarrow$ Matter flow from I to II.

$\Rightarrow$ Matter flows from High μ to low μ.

4-4. chemical Equilibrium.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

$$0 \rightleftharpoons -2H_2 - O_2 + 2H_2O$$

$$0 \rightleftharpoons \sum_j \underbrace{\nu_j}_{\text{coffecient}} \underbrace{A_j}_{\text{chemical species}}$$

$$dS = 0 = \sum_{j=1}^{r} \left(\frac{\partial S}{\partial N_j} \right) dN_j = -\sum_{j=1}^{r} \left(\frac{\mu_j}{T} \right) dN_j$$

$\frac{\partial S}{\partial N_j} \to -\frac{\mu_j}{T}$

$$\frac{\partial S}{\partial x_j} = -\frac{P_j}{T} \to \left(\frac{\partial U}{\partial x_j} \right)$$

$$N_j = \tilde{N} \cdot \nu_j \longrightarrow dS = -\sum_{j=1}^{r} \mu_j \nu_j \frac{d\tilde{N}}{T}$$

$=0$

$$\Rightarrow \sum_{j=1}^{r} \mu_j \nu_j = 0$$

e.g., $CO_2 + H_2 \rightleftharpoons CO + H_2O$

$\mu_{CO_2} + \mu_{H_2} = \mu_{CO} + \mu_{H_2O}$ ✓

$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$

$\mu_{CO} + \frac{1}{2}\mu_{O_2} = \mu_{CO_2}$ ✓

Obj #3 Basic Math Background

1. Partial Derivatives (P.D.)
2. Expansions of Functions (Multivariable)
3. Composite Functions.
4. Implicit Functions.

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1. P.D.

Def. Function : continuous & multivariable.

i.e. $\psi = \psi(x, y, z)$

*. $\left(\frac{\partial \psi}{\partial x}\right)_{y,z}$ — depends on x. AND on the values at which y & z are fixed.

*. if $\left(\frac{\partial \psi}{\partial x}\right)_{y,z}$ is continuous, it could be

differentiated again. to yield 2^{nd} order.

P.D. of ψ.

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\right)_{y,z} ; \quad \left(\frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\right)_{x,z} ; \quad \left(\frac{\partial}{\partial z}\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\right)_{x,y}.$$

↓

likewise $\left(\frac{\partial \psi}{\partial y}\right)_{x,z}$ . . .

what about $\left(\frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\right)_{x,z} \overset{?}{=}$ vs $\left(\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial y}\right)_{x,z}\right)_{y,z}$?

$\ast$ symmetry & state Function.

For certain ψ. the order of Diff. does NOT affect the outcome. i.e.

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right)_{y}\right)_{x} = \left(\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial y}\right)_{x}\right)_{y}$$

then, ψ is a so-called state function.

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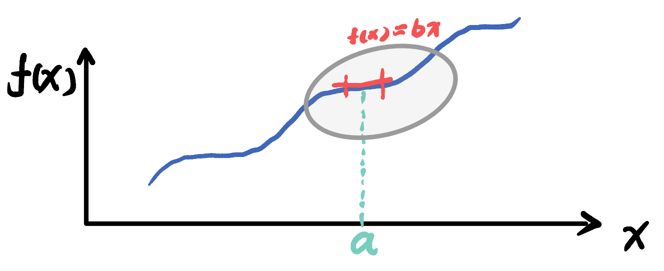
2. Expansion of Functions

*.



$$f(x)_a = f(a) + \frac{1}{1!}\left(\frac{df}{dx}\right)_{x=a}(x-a)$$

$$\frac{1}{2!}\left(\frac{d^2f}{dx^2}\right)_{x=a}(x-a)^2$$

$$\vdots$$

$$\frac{1}{n!}\left(\frac{d^nf}{dx^n}\right)_{x=a}(x-a)^n$$

For multivariable.

→ $\psi(x, y, z) \rightarrow \psi(x+dx, y+dy, z+dz)$

$$= \psi(x, y, z) + \underbrace{\left(\frac{\partial\psi}{\partial x}dx + \frac{\partial\psi}{\partial y}dy + \frac{\partial\psi}{\partial z}dz\right)}_{1^{st}\text{ order}}$$

Now, let $d^n\psi = \left(\frac{\partial}{\partial x}dx + \frac{\partial}{\partial y}dy + \frac{\partial}{\partial z}dz\right)^n \psi(x, y, z)$

then, → $\psi(x+dx, y+dy, z+dz)$

$$= \psi(x, y, z) + \frac{1}{1!}d\psi + \frac{1}{2!}d^2\psi + \cdots + \frac{1}{n!}d^n\psi$$

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3. Composite Functions

$f(x)$, $g(x)$, $h(x)$

$h(x) = g(f(x))$ → composite

chain rule :

$$\boxed{\frac{dh}{dx} = \frac{d}{dx}(g(f(x))) = \frac{dg}{df}\cdot\frac{df}{dx}}$$

$$\boxed{\begin{aligned}&\text{if} \quad h(x) = f_1(f_2(f_3(\cdots(f_n(x)\cdots)\\ &\rightarrow \frac{dh(x)}{dx} = \frac{df_1}{df_2} \cdot \frac{df_2}{df_3} \cdots \frac{df_n}{dx}\end{aligned}}$$

*. multivariable. $\psi = \psi(x, y, z)$

$$d\psi = \underline{\left(\frac{\partial \psi}{\partial x}\right)}_{yz} dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \psi}{\partial z}\right)_{xy} dz.$$

<1.> if $\underline{x = x(u)}$, $y = y(u)$. $z = z(u)$

$$\psi(x(u), y(u), z(u))$$

$$d\psi = \underline{\left[\left(\frac{\partial \psi}{\partial x}\right)_{yz} \left(\frac{dx}{du}\right) + \left(\frac{\partial \psi}{\partial y}\right)_{xz} \left(\frac{dy}{du}\right) + \left(\frac{\partial \psi}{\partial z}\right)_{xy} \left(\frac{dz}{du}\right) \right] du}$$

<2> if $x = x(u, v)$, $y = y(u, v)$, $z = z(u, v)$

$$dx = \left(\frac{\partial x}{\partial u}\right)_v du + \left(\frac{\partial x}{\partial v}\right)_u dv$$

likewise, for dy & dz.

$$\frac{\partial \psi}{\partial u}$$

$$d\psi \rightarrow = \underline{[\qquad \qquad] du}$$

$$+ [\qquad \qquad] dv$$

$$\frac{\partial \psi}{\partial v}$$

4. Implicit Function.

For $\psi = \psi(x, y, z)$, if $\psi = \text{const.}$

x, y, z are NOT independent. $\psi(x, y, z)$ is implicit function.

$z = z(x, y)$

*. Let $d\psi = 0$ ($\psi = \text{const}$)

$$\rightarrow \quad d\psi = 0 = \left(\frac{\partial \psi}{\partial x}\right)_{yz} dx + \left(\frac{\partial \psi}{\partial y}\right)_{xz} dy + \left(\frac{\partial \psi}{\partial z}\right)_{xy} dz$$

Now, consider $dz = 0$

$$\rightarrow \quad 0 = \left(\frac{\partial \psi}{\partial x}\right)_{yz} dx + \left(\frac{\partial \psi}{\partial y}\right)_{xz} dy$$

divided by dx

$$\Rightarrow \quad 0 = \left(\frac{\partial \psi}{\partial x}\right)_{yz} + \left(\frac{\partial \psi}{\partial y}\right)_{xz} \left(\frac{\partial y}{\partial x}\right)_{\psi, z}$$

$$\rightarrow \quad \boxed{\underline{\left(\frac{\partial y}{\partial x}\right)_{\psi, z}} = -\frac{(\partial \psi / \partial x)_{y, z}}{(\partial \psi / \partial y)_{x, z}}}$$

relation of x, y determined by the values at which ψ & z hold.

likewise, if we let $dy = 0$

$$\rightarrow \quad \boxed{\left(\frac{\partial z}{\partial x}\right)_{\psi, y} = -\frac{(\partial \psi / \partial x)_{yz}}{(\partial \psi / \partial z)_{xy}}}$$

if $dx = 0$

$$\rightarrow \boxed{\left(\frac{\partial z}{\partial y}\right)_{\psi, x} = -\frac{(\partial \psi/\partial y)_{x,z}}{(\partial \psi/\partial z)_{x,y}}}$$

Now, Let $dz = 0$

$$\rightarrow 0 = \left(\frac{\partial \psi}{\partial x}\right)_{yz} dx + \left(\frac{\partial \psi}{\partial y}\right)_{xz} dy$$

divided by dy

$$\rightarrow \left(\frac{\partial \psi}{\partial x}\right)_{y,z} \left(\frac{\partial x}{\partial y}\right)_{\psi,z} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_{\psi,z} = -\frac{(\partial \psi/\partial y)_{xz}}{(\partial \psi/\partial x)_{y,z}}}$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_{\psi,z} = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_{\psi,z}}} \;*$$

$$* \Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_{\psi,z} \left(\frac{\partial y}{\partial z}\right)_{\psi,x} \left(\frac{\partial z}{\partial x}\right)_{\psi,y} = -1}$$

→ " cyclic rule "

Obj. 4. Mathmatical Properties of Fundamental Equations.

1. Euler Equation.
2. Gibbs – Duhem Relation.
3. Structure of thermodynamic Formulism.
4. E.O.S. (and Fundamental Eq.) for common sys.