Extensive functions + Gibbs-Duhem Equation

$E(\lambda S, \lambda X) = \lambda E(S, X)$ λ Is a scaling parameter

E is 1st order homogenous function of *S*

$f(x_1, x_n)$ is a 1st order homogenous function of $x_1, \ldots, x_n$

let $\mu_i = \lambda x_i$

$$f\left(\mu_i, \ldots, \mu_n\right) = \lambda f\left(x_1, \ldots, x_n\right)$$

$$\left(\frac{\partial f}{\partial \lambda}\right)_{x_i} = f\left(x_1, \ldots, x_n\right)$$

$$df\left(\mu_1, \ldots, \mu_n\right) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial \mu_i}\right)_{\mu_j} d\mu_i$$

$$\left(\frac{df}{d\lambda}\right)_{x_i} = \sum \left(\frac{\partial f}{\partial \mu_i}\right)_{\mu_j} \left(\frac{\partial \mu_i}{\partial \lambda}\right)$$

$$f\left(x_1, \ldots x_n\right) = \sum \left(\frac{\partial f}{\partial \mu_i}\right)_{\mu_j} x_i,$$

$$f\left(x_1,\ldots x_n\right)=\sum\left(\frac{\partial f}{\partial \mu_i}\right)_{\mu_j} x_i,$$ for all λ

$$\downarrow \lambda=1$$

$$\boxed{\mathrm{f}\left(x_1,\ldots,x_n\right)=\sum\left(\frac{\partial f}{\partial x_i}\right)_{x_j} x_i} \longleftarrow$$

Euler's theorem for 1st order homogenous equation

$$E = E(S, X)$$

$$E = \left(\frac{\partial E}{\partial S}\right)_X S + \left(\frac{\partial E}{\partial X}\right)_S X = TS + f \cdot X$$ ⟵ from Euler's Equation

$$dE = TdS - pdV + \Sigma \mu_i dn_i$$

$$E = TS - pV + \Sigma \mu_i n_i$$

$$dE = TdS - SdT - pdV - Vdp + \Sigma \mu_i dn_i + \Sigma n_i d\mu_i$$

$$\Rightarrow \boxed{SdT - Vdp + \Sigma n_i d\mu_i = 0}$$ | Gibbs-Duhem Equation

$$G = E - TS + pV$$

$$G = \left[TS - pV + \Sigma\mu_i n_i\right] - TS + pV$$

$$G = \Sigma\mu_i n_i$$

for a one-component system

$$G = \mu n$$

In general $X(T, p, n_1, \ldots, n_r) = \sum_{i=1}^{r} x_i n_i$

extensive funct

partial molar *x*'s

Intensive functions

are <u>zeroth</u> order functions of extensive variables

e.g., $p = p\left(S,V,n_1,\ldots,n_r\right) = p\left(\lambda S,\lambda V,\lambda n_1,\ldots,\lambda n_r\right)$

This is true for any λ. Let

$$\frac{1}{\lambda} = n_1 + n_2 + \ldots + n_r = n$$

$$p = p\left(S/n, V/n, x_1,\ldots, x_n \quad\right)$$

$$p = \left(S/n,\ V/n,\ x_1,\ldots,x_{r-1},1-x_1-,\ldots,-x_{r-1} \quad\right)$$

2+r variables need to establish extensive variable

1+r variables needed to specify an intensive variable