**Calculus of Thermodynamics**

This unit covers the relationship between the fundamental extensive properties such as internal energy, entropy, enthalpy, Helmholtz free energy and Gibbs free energy. We will cover the derivation of each function and their application to problems.

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| ***Internal energy*** | dU=TdS-PdV+$μ$dN |
| ***Enthalpy*** | dH=TdS+VdP+$ μ$dN |
| ***Entropy*** | dS= $\frac{dU}{T}+$ $\frac{PdV}{T}- \frac{μdN}{T}$ |
| ***Gibbs Free Energy*** | dG= -SdT+VdP+$μ$dN |
| ***Helmholtz Free Energy*** | dA=-SdT-PdV+$μ$dN |

**Maxwell’s relations**

According to the expression given below:

$$dφ=M \left(x,y\right)dx+N \left(x,y\right)dy$$

$$\left(\frac{∂M}{∂y}\right)\_{x}=\left(\frac{∂M}{∂x}\right)\_{y}$$

This relation will be useful to derive the followings:

$$\left(\frac{∂T}{∂\hat{V}}\right)\_{\hat{S}}=-\left(\frac{∂P}{∂\hat{S}}\right)\_{\hat{V}}$$

$$\left(\frac{∂T}{∂P}\right)\_{\hat{S}}=\left(\frac{∂\hat{V}}{∂\hat{S}}\right)\_{P}$$

$$\left(\frac{∂P}{∂T}\right)\_{\hat{V}}=\left(\frac{∂\hat{S}}{∂\hat{V}}\right)\_{T}$$

$$\left(\frac{∂\hat{V}}{∂T}\right)\_{P}=-\left(\frac{∂\hat{S}}{∂P}\right)\_{T}$$

Above equations are called the ***Maxwell equations***.

Heat capacity at constant V and P, isothermal compressibility and thermal expansivity are defined as follows:

$\hat{C\_{V}}=\left(\frac{d\hat{U}}{dT}\right)\_{\hat{V}}$ and $\hat{C\_{P}}=\left(\frac{d\hat{H}}{dT}\right)\_{P}$

Thermal expansion coefficient gives you the change of volume with temperature at constant pressure per unit volume

$$β=\frac{1}{\hat{V}}\left(\frac{\hat{V}}{T}\right)\_{P}$$

On the other hand, isothermal compressibility gives you the change of volume with pressure at constant temperature per unit volume

$$κ=-\frac{1}{\hat{V}}\left(\frac{\hat{V}}{P}\right)\_{T}$$

* In order to relate the partial derivatives of Maxwell relations and do the calculations in an easier way, the following mathematical rules can be used.

In case of a function of f(x,y) which can be written:

$$df=\left(\frac{∂f}{∂x}\right)\_{y}dx+\left(\frac{∂f}{∂y}\right)\_{x}dy$$

When both sides are differentiated with respect to f at constant y, we get:

$$1=\left(\frac{∂f}{∂x}\right)\_{y}\left(\frac{∂x}{∂f}\right)\_{y}$$

$$\left(\frac{∂f}{∂x}\right)\_{y}= \frac{1}{\left(\frac{∂x}{∂f}\right)\_{y}}$$

The last equation is called the ***inverse rule***.

* $df=\left(\frac{∂f}{∂x}\right)\_{y}dx+\left(\frac{∂f}{∂y}\right)\_{x}dy$

Differentiating the above equation with respect to y keeping f constant will yield

$$0=\left(\frac{∂f}{∂x}\right)\_{y}\left(\frac{∂x}{∂y}\right)\_{f}+\left(\frac{∂f}{∂y}\right)\_{x}$$

 Applying inverse rule turns the equation into

$$0=\left(\frac{∂f}{∂x}\right)\_{y}\left(\frac{∂x}{∂y}\right)\_{f}+\frac{1}{\left(\frac{∂y}{∂f}\right)\_{x}}$$

Multiplication of both sides by $\left(\frac{∂y}{∂f}\right)\_{x}$finally gives

$$0=\left(\frac{∂f}{∂x}\right)\_{y}\left(\frac{∂x}{∂y}\right)\_{f}\left(\frac{∂y}{∂f}\right)\_{x}+1$$

$$\left(\frac{∂f}{∂x}\right)\_{y}\left(\frac{∂x}{∂y}\right)\_{f}\left(\frac{∂y}{∂f}\right)\_{x}=-1$$

The last equation is called the ***triple product rule.***

Reference:

Ismail Tosun, “The Thermodynamics of Phase and Reaction Equilibria”, 2012, Elsevier.