# Van't Hoff and Maxwell Relations

## 1 Overview

Recall different energy expressions including chemical potential:

$$dU = TdS - pdV + \sum_{i=1}^{k} \mu_i dn_i \tag{1}$$

$$dH = TdS + Vdp + \sum_{i=1}^{k} \mu_i dn_i \tag{2}$$

$$dG = Vdp - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{3}$$

$$dF = -pdV - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{4}$$

Then for the four basic TD properties (T, p, V, S), we have:

$$T = \frac{\partial U}{\partial S}|_{V,n_i} = \frac{\partial H}{\partial S}|_{p,n_i} \tag{5}$$

$$p = -\frac{\partial U}{\partial V}|_{S,n_i} = -\frac{\partial F}{\partial V}|_{T,n_i} \tag{6}$$

$$V = \frac{\partial H}{\partial p}|_{S,n_i} = \frac{\partial G}{\partial p}|_{T,n_i} \tag{7}$$

$$S = -\frac{\partial G}{\partial T}|_{p,n_i} = -\frac{\partial F}{\partial T}|_{V,n_i} \tag{8}$$

## 2 Van't Hoff Relation (first step)

This is only a brief introduction, details in later chapter.

$$\begin{aligned}\frac{\partial}{\partial T}(\frac{G}{T})_{p,n_i} &= \frac{\partial G}{\partial T}|_{p,n_i}\frac{1}{T} + G\frac{\partial(1/T)}{\partial T}|_{p,n_i} \\ &= -S\frac{1}{T} + G(-\frac{1}{T^2}) \\ &= (-TS - G)\frac{1}{T^2} \\ &= \frac{-H}{T^2}\end{aligned} \tag{9}$$

## 3 Maxwell Relations

Previously we already know:

$$dF = x_1 dy_1 + x_2 dy_2 + ... + x_i dy_i \tag{10}$$

$$x_1 = \frac{\partial F}{\partial y_1}|_{y_{j\neq 1}} \tag{11}$$

Now we introduce **reciprocity relation**:

$$\frac{\partial x_i}{\partial y_j}|_{y_{k\neq j}} = \frac{\partial x_j}{\partial y_i}|_{y_{k\neq i}} \tag{12}$$

Then we can derive the **Maxwell relations**. From:

$$dU = TdS - pdV + \sum_{i=1}^{k}\mu_i dn_i \tag{13}$$

We can get:

$$\frac{\partial T}{\partial V}|_{S,n_i} = -\frac{\partial p}{\partial S}|_{V,n_i} \tag{14}$$

Then from:

$$dH = TdS + Vdp + \sum_{i=1}^{k}\mu_i dn_i \tag{15}$$

We can get:

$$\frac{\partial T}{\partial p}|_{S,n_i} = \frac{\partial V}{\partial S}|_{p,n_i} \tag{16}$$

From:

$$dG = Vdp - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{17}$$

We can get:

$$\frac{\partial V}{\partial T}|_{p,n_i} = -\frac{\partial S}{\partial p}|_{T,n_i} \tag{18}$$

We can also include chemical potential:

$$\frac{\partial \mu_i}{\partial p}|_{T,n_i,n_j} = \frac{\partial V}{\partial n_i}|_{T,p,n_{j\neq i}} \tag{19}$$

Similarly, from:

$$dF = -pdV - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{20}$$

We can get:

$$\frac{\partial p}{\partial T}|_{V,n_i} = \frac{\partial S}{\partial V}|_{T,n_i} \tag{21}$$

And:

$$\frac{\partial \mu_i}{\partial T}|_{V,n_i,n_j} = -\frac{\partial S}{\partial n_i}|_{T,V,n_{j\neq i}} \tag{22}$$