まとめ　4. 熱力学的関係式，物質量と化学ポテンシャル

熱力学的関係式：

$$\frac{d'Q}{T} = dS, \qquad d'W = pdV \qquad \text{準静的過程}$$

$$\therefore\ dU = TdS - pdV \qquad \text{（第一法則）}$$

自然な熱力学的変数：

$$U = U(S, V, N)$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p$$

化学ポテンシャル：

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

$$dU = TdS - pdV + \mu dN$$

$$\frac{d'Q}{T} = dS, \qquad d'W = pdV - \mu dN \qquad \text{準静的過程}$$

※ $-\mu dN$： 準静的に物質量 N を増減するときに要する仕事，または，内部エネルギーの変化

Maxwell 関係式 (積分可能条件)：

$$\begin{aligned} dS &= \frac{dU + pdV}{T} \\ &= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \end{aligned}$$

$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$ より

$$\frac{\partial}{\partial V}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right\} = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\right\}$$

$$\therefore \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\therefore \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \text{(Maxwell 関係式)}$$