

## まとめ 7. 熱力学的関係式, 物質と化学ポテンシャル

熱力学の基本方程式：

$$\frac{d'Q}{T} = dS, \quad d'W = pdV \quad \text{準静的過程}$$
$$\therefore dU = TdS - pdV \quad (\text{第一法則} + \text{第二法則})$$

自然な熱力学的変数：

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

化学ポテンシャル：

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$
$$dU = TdS - pdV + \mu dN$$
$$\frac{d'Q}{T} = dS, \quad d'W = pdV - \mu dN \quad \text{準静的過程}$$

※  $+\mu dN$ ：準静的に物質  $N$  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)：

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

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

$$\frac{\partial}{\partial V} \left\{ \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \right\} = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[ \left(\frac{\partial U}{\partial V}\right)_T + p \right] \right\}$$
$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$
$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (\text{Maxwell 関係式})$$