〈マクスウェルの関係式〉

$$\frac{d'Q}{T}=dS \qquad d'Q=TdS \quad —①$$

熱力学第一法則より

$$dU=d'Q+d'W \quad —② \qquad d'W=-pdV \quad —③$$

$$dU=d'Q-pdV=TdS-pdV$$

$$TdS=dU+pdV$$

$$dS=\frac{1}{T}dU+\frac{p}{T}dV \quad —④$$

$S(U,V)$

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_V=\frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_U=\frac{P}{T}}$$

$dU=TdS-pdV$ より

$U(S,V)$

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_V=T \qquad \left(\frac{\partial U}{\partial V}\right)_S=-P}$$

$$H=U+PV \quad —⑤$$

$$dH=dU+PdV+VdP$$

$$=TdS-\cancel{pdV}+\cancel{pdV}+Vdp$$

$$dH=TdS+Vdp \quad —⑥$$

$H(P,S)$

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_p=T \qquad \left(\frac{\partial H}{\partial p}\right)_S=V}$$

$$\left(\frac{\partial H}{\partial P}\right)$$

$$F=U-TS$$

$$dF=dU-TdS-SdT$$

$$=TdS-pdV-TdS-SdT$$

$$dF=-pdV-SdT$$

$$\boxed{\left(\frac{\partial F}{\partial V}\right)_T = -p \qquad \left(\frac{\partial F}{\partial T}\right)_V = -S} \qquad F(T,V)$$

$$G = F + pV$$

$$dG = dF + pdV + Vdp = \cancel{-pdV} - SdT + \cancel{pdV} + Vdp$$

$$dG = -SdT + Vdp$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V} \qquad G(p,T)$$

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_V = \frac{\partial}{\partial U}\left(\frac{\partial S}{\partial V}\right)_U \qquad \frac{\partial}{\partial V}\left(\frac{1}{T}\right) = \frac{\partial}{\partial U}\left(\frac{p}{T}\right)$$

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

$$\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S = \frac{\partial}{\partial p}(T) = \frac{\partial}{\partial S}(V)$$

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

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T \qquad \frac{\partial}{\partial p}(-S) = \frac{\partial}{\partial T}(V)$$

$$\boxed{-\frac{\partial p}{\partial S} = \frac{\partial T}{\partial V} \qquad \frac{\partial T}{\partial p} = \frac{\partial V}{\partial S} \qquad \frac{\partial p}{\partial T} = \frac{\partial S}{\partial V} \qquad -\frac{\partial S}{\partial p} = \frac{\partial V}{\partial T}}$$

マクスウェルの関係式

$$\begin{array}{ccc} T & = & V \\ | & & | \\ p & = & S \end{array}$$

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— は (−)