内圧、膨張率、等温圧縮率と熱容量

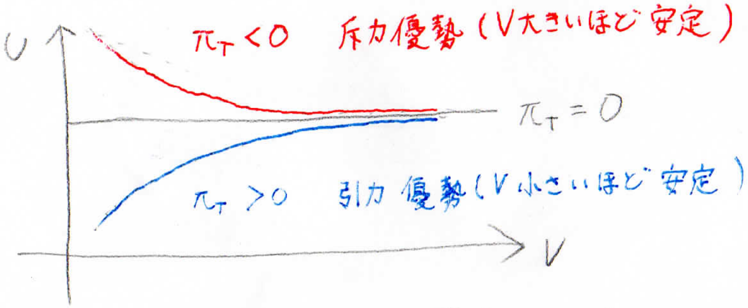
☆ 内圧

$U(V,T)$の全微分

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\pi_T \equiv \left(\frac{\partial U}{\partial V}\right)_T$$ 内圧（圧力の次元）

π_Tは分子間相互作用のパラメータになる



分子間相互作用がない理想気体では、

$$\pi_T = 0 \longrightarrow dU = C_V dT$$

☆ 膨張率、等温圧縮率

膨張率 $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

等温圧縮率 $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

$dU = \pi_T dV + C_V dT$ より

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T\left(\frac{\partial V}{\partial T}\right)_p + C_V \underbrace{\left(\frac{\partial T}{\partial T}\right)_p}_{1}$$

$$= \pi_T \alpha V + C_V$$

理想気体のとき、

$$\pi_T = 0$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$H = U + pV$　$C_p = \left(\frac{\partial H}{\partial T}\right)_p$ より

$$C_p - C_V = \left[\frac{\partial (U+pV)}{\partial T}\right]_p - \left(\frac{\partial U}{\partial T}\right)_p$$

$$= \left[\frac{\partial (pV)}{\partial T}\right]_p$$

$$= nR$$ （$pV = nRT$ より）

Mayer の式（理想気体で成立）

$$\boxed{C_p - C_V = nR}$$

一般的には、$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T\left(\frac{\partial V}{\partial T}\right)_p + C_V$ より、

$$C_p - C_V = \left[\frac{\partial (U+pV)}{\partial T}\right]_p - \left(\frac{\partial U}{\partial T}\right)_p + \pi_T\left(\frac{\partial V}{\partial T}\right)_p$$

$$= p\left(\frac{\partial V}{\partial T}\right)_p + V\underbrace{\left(\frac{\partial p}{\partial T}\right)_p}_{0} + \pi_T\left(\frac{\partial V}{\partial T}\right)_p$$

$$= (p + \pi_T)\alpha V$$

エントロピー S として、熱力学基本式 $dU = TdS - pdV$

マクスウェルの関係式 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$= T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial p}{\partial T}\right)_V} - p\underbrace{\left(\frac{\partial V}{\partial V}\right)_T}_{1}$$

$$p + \pi_T = T\left(\frac{\partial p}{\partial T}\right)_V$$

$$C_p - C_V = \alpha T V \left(\frac{\partial p}{\partial T}\right)_V$$

体積 $V(p, T)$ の全微分

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

$dV = 0$ のとき.

$$\left(\frac{\partial V}{\partial p}\right)_T dp = -\left(\frac{\partial V}{\partial T}\right)_p dT$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T}$$

オイラーの連鎖式

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$$

$$= \frac{\alpha}{\kappa_T}$$

$$\boxed{C_p - C_V = \frac{\alpha^2 T V}{\kappa_T}}$$