§1 温度

熱力学

物体の状態 T, V, P

↓

内部エネルギー , 力学エネルギー

↑ 温度 ↑ 速度(運動E), 位置(位置E)

熱平衡になったときの物理量は、状態方程式で表される.

熱力学第零法則

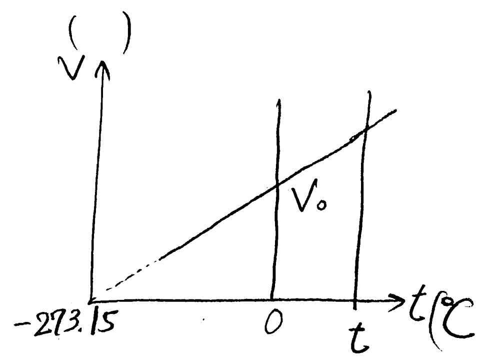
A−B 熱平衡, A−C 〃 → B−C 熱平衡.

便宜的温度計

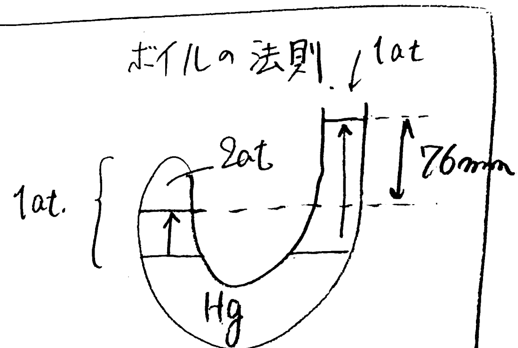
標準温度計

↓

理想気体温度計



ボイルの法則



$pV = $一定

シャルルの法則

$$V = at + b$$

$$= b\left(1 + \frac{a}{b}t\right)$$

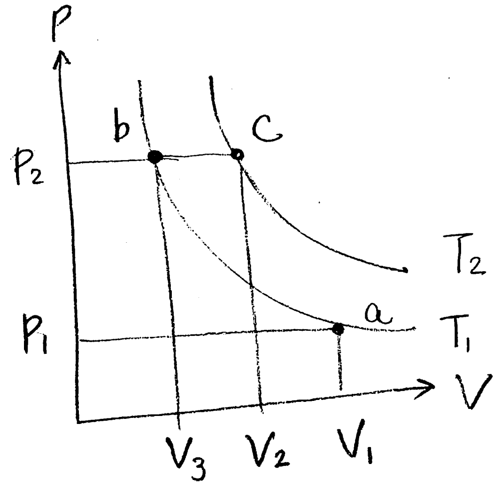
$$= V_0\left(1 + \frac{t}{273.15}\right)$$

$$= V_0 \cdot \frac{273.15 + t}{273.15}$$

ここで $T = \underbrace{273.15}_{T_0} + t$ とすると.

$$V = V_0 \cdot \frac{T}{T_0}$$

$$\therefore \frac{V}{T} = \frac{V_0}{T_0} = \text{一定}$$



$a \to b$ (ボイル)

$$P_1 V_1 = P_2 V_3$$

$b \to c$ (シャルル)

$$\frac{V_3}{T_1} = \frac{V_2}{T_2} \quad \therefore V_3 = \frac{T_1}{T_2} V_2$$

上式に代入すると、

$$P_1 V_1 = P_2 \cdot \frac{T_1}{T_2} V_2$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \underbrace{R\,(\text{一定})}$$

気体定数

8.3144 (J/K·mol)

(≈ 2 cal/K·mol)

§1.3 状態方程式、

$V = V(p, T)$	(1.8)
$T = T(p, V)$	(1.9)
$f(p, T, V) = 0$	状態方程式

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \qquad (1.11)$$

Tを一定に

圧縮率 K

$$\frac{dV}{V} = \boxed{-K} dp$$

等温圧縮率

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

const.

圧力を上げると体積は減る.

(1.11) 式は、$T = const.$ ならば、

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

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

$$\therefore K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad (1.14)$$

K_T の逆数 : $k_T = \frac{1}{K_T}$ 等温体積弾性率

$$k_T = \frac{1}{K_T} = \frac{-V}{\left(\frac{\partial V}{\partial p}\right)_T} = -V\left(\frac{\partial p}{\partial V}\right)_T \quad (1.15)$$

$$dp = -k_T \frac{dV}{V}$$

弾性率 E

$$\underset{\text{応力}}{d\sigma} = E_T \underset{\text{ひずみ}}{d\varepsilon}$$

バネ定数

$$\underset{\text{荷重}}{\underline{dF}} = K_T \underset{\text{変位}}{\underline{dl}}$$

体膨張率 α

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

熱圧力係数 β

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

(1.11) で $\boxed{dV = 0}$

$$0 = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

dT で割る

$$\therefore 0 = \left(\frac{\partial V}{\partial p}\right)_T \boxed{\left(\frac{\partial p}{\partial T}\right)_{\boxed{V}}} + \left(\frac{\partial V}{\partial T}\right)_p$$

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

$$\therefore \boxed{\beta} = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$$

ここで $\left(\frac{\partial V}{\partial T}\right)_p = \alpha V$ (1.16)

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{V}{k_T} \quad (1.15)$$

$$\therefore \beta = -\frac{\alpha V}{-\left(\frac{V}{k_T}\right)} = \alpha k_T = \frac{\alpha}{K_T} \quad (1.19)$$

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

$$\therefore \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \quad (1.18)$$

§ 1.4 気体の状態方程式

ファンデルワールスの状態方程式 (1.21) の T_c, P_c, v_c を求める

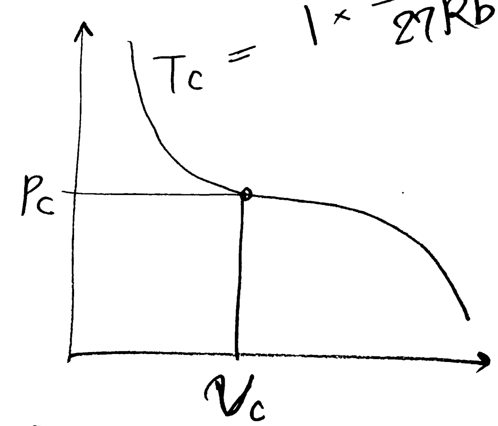
$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{———} \; ①$$

$T = T_c$ (臨界温度) では 曲線の接線が0で 変曲点でもあるから、

$$\left(\frac{\partial p}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT_c}{(v_c-b)^2} + \frac{2a}{v^3} = 0$$

$$T_c = 1 \times \frac{8a}{27Rb}$$



$$\therefore \frac{RT}{(v_c-b)^2} = \frac{2a}{v_c^3} \quad \text{———} \; ②$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v_c-b)^3} - \frac{6a}{v^4} = 0$$

$$\therefore \frac{2RT}{(v_c-b)^3} = \frac{6a}{v^4} \quad \text{———} \; ③$$

① ÷ ② より、

$$\frac{v_c-b}{2} = \frac{v_c}{3}$$

$$\therefore v_c = 3b$$

これを②に代入

$$T_c = \frac{8a}{27Rb}.$$

①に代入

$$P_c = \frac{a}{27b^2}$$

1 mol

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT$$

n mol のときは $V = nv$

$$\left(p+\frac{n^2a}{(nv)^2}\right)\left(\frac{1}{n}\right)(nv-nb) = RT$$

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$